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SHEARING PHENOMENA AT HIGH PRESSURES, PARTICULARLY IN INORGANIC COMPOUNDS

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Introduction

Two papers have already been published dealing with shearing phenomena at high pressures.[1] The first of these outlined the general nature of the phenomena and described especially the experimental results for the elements. The second described qualitatively a number of phenomena which it seemed to me must be of significance for the speculations of the geologist, without, however, any attempt to make the detailed geological application. In this present paper I propose in the first place to consider several matters of technique and detail for which there was no opportunity in the previous papers, then to describe several new kinds of experiment, such as investigations of the effect of speed of deformation, and finally to summarize as briefly as possible the essential features of new measurements on the shearing of some 250 new substances, mostly inorganic compounds examined during the last year.

Apparatus and Method

The general nature of the apparatus has been indicated in the previous papers. It consists of two cylindrical steel blocks B provided with short cylindrical bosses, called hereafter the "pistons," pressed against a block C of rectangular section, hereafter called the "anvil," mounted between the two pistons. The material under investigation takes the form of a thin disc, indicated at A, between piston and anvil. The pistons are pressed against the anvil with any desired pressure by a hydraulic press, and while pressure is applied the anvil is rotated between the pistons, usually by a handle pushed by hand. Friction

on the large base of the piston is sufficient to prevent the piston rotating with the anvil. The force required to maintain rotation is measured with a strain gauge so mounted as to measure the bending of the handle, which is made of a piece of flat automobile spring steel, about 8 mm. thick, 6 cm. wide, and 1 m. long.

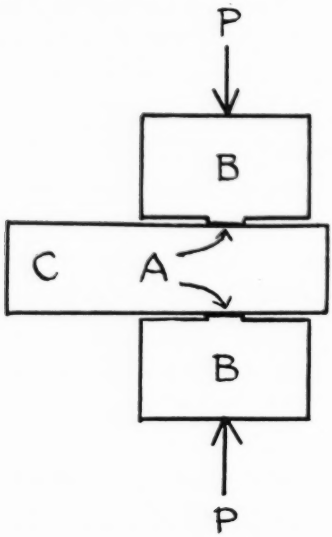

FIGURE 1. General scheme of apparatus for combining shearing stress with pressure.

In order to reach the highest pressures, which in these experiments were almost always about 50000 kg/cm^2, the steel of piston and anvil must have special properties. The steel found best was a chrome steel used for making ball bearings. The particular grade used was obtained from the Ludlum Steel Co. and is sold by them under the trade name of "Teton." It was hardened by quenching into oil from 1600° F, and was used without drawing, except for heating in boiling water to relieve strains. It had a hardness on the Rockwell C scale of 64–66. Hardening was done in a gas furnace, bringing the steel rapidly to temperature, and quenching as soon as equilibrium temperature was reached. The slower heat obtained with a large electric furnace to my surprise proved not to be favorable, there being a high

percentage of fractures during hardening when the electric furnace was used. The steel as it comes from the mill is not perfectly uniform; some bars are incapable of giving the hardness required, so that it was necessary to obtain a number of bars, specified to be from different meltings, and select the better ones. The pistons were machined to size before quenching. The warping during hardening was not sufficiently serious to disturb the external cylindrical surface, and this was left untouched after hardening. The two plane ends, that is, the large flat base and the face of the boss (the piston) were ground after hardening. This was done with a surface grinder, taking care to have the faces accurately parallel, and using such a grade of wheel and fineness of cut as to leave the surface in a condition almost of polish. The wheel was freshly dressed with a diamond before grinding a batch of pistons or anvils.

If the piston is not too much damaged by an experiment, it may be reground and used again. The usual form of damage to the piston consists in shearing off little triangular prisms from the edge. Other sorts of damage also occur, such as rounding of the edge by slipping, the slip lines appearing as circles concentric with the edge, and somewhat rarely by the appearance of deep radial cracks near the periphery running through to the edge. If the steel is too soft, the piston upsets, becoming larger in diameter. In addition to these kinds of damage, and much less serious, the surface might be scratched in various ways or polished or burnished when harder materials were sheared. The nature of the damage is characteristic of the material being sheared. It would be interesting to find a detailed explanation of the dependence of the nature of the damage on the properties of the material, but at present this appears hopelessly difficult. Regrinding was not attempted unless complete recovery of the original perfect geometrical figure was possible by removing not more than 0.010 cm from the face of the piston. The average piston allowed two or three regrindings, and there have been extreme examples of as many as seven. The damage to the anvil is, as might be expected, much less severe than that to the piston; the effect consists of a permanent depression and scratching or tearing of the surface. Removal of 0.0025 cm by grinding was sufficient in nearly all cases to give a completely fresh surface. The anvil was used four times without regrinding, the locality of contact with the piston being shifted along from one experiment to the next. The permanent depression produced in a new anvil is larger at first than after it has been used and the surface ground off a few times. The steel becomes hardened by

cold working so that eventually very little impression is made in it by the piston. However, the properties of the steel must be just right; more than half the anvils used split after having been resurfaced a few times, the fracture taking the form of a characteristic conical button pushed by the piston into the bulk of the anvil, splitting it like a wedge. A good anvil can be reground until too thin to fit the apparatus.

The pistons were pressed against the anvil by a hydraulic press very similar to that used in much of my high pressure work.[2] The piston of the press is 3.5 inches in diameter, and is actuated by a hand pump capable of delivering 1000 kg/cm.[2] The press is made with great care so that all parts shall be in accurate alignment. The piston of the press is packed according to the principle of the "unsupported area." The packing material is "Duprene" 0.25 inch thick. Duprene has been found markedly superior to ordinary soft rubber for this purpose, the friction being materially less and the wearing qualities much better. The Duprene is retained by conical rings of soft brass, instead of by red fibre washers, as in my early design. This has the effect of further reducing friction. The pressure on the pistons was calculated directly from the area of the piston of the press and the pressure acting on it, making no allowance for friction. Friction was not more than 1 or 2 per cent. This was checked in two ways; by measuring the extension of the tie rods of the press with a strain gauge during increasing and decreasing pressure, and by mounting the press against another similar press in such a way that the piston of one press pushes the piston of the other press, the pressure thereby produced in the fluid of the second press being determined as a function of the driving pressure in the fluid of the first.

The pressure of the piston of the hydraulic press was measured with a dead weight gauge, with piston 0.25 inch in diameter. A series of equi-spaced weights was provided, so that pressure could be increased in regular steps by adding successive weights. Usually 25 equal steps were used in reaching 50000 kg/cm^2 on the pistons, which corresponded to about 250 kg/cm^2 on the piston of the hydraulic press. During a reading the pressure on the piston was therefore constant to a high degree of precision, in spite of any small displacement that the piston of the press might be experiencing. This procedure for determining and fixing the pressure was very much more satisfactory than determining the pressure from the Bourdon gauge of the hand pump.

In assembling the apparatus a special form has to be provided to

hold the pistons and the anvil accurately in line. This was a split affair, straddling the anvil, and held together with screws which could be removed after everything was in place and enough pressure had been applied to keep things together. It is not necessary to describe this form in further detail.

The specimen, in the form of discs at A (Figure 1), was prepared in various ways. In the case of some metals, thin discs of sheet metal could be punched out. Most materials investigated, however, were initially in the form of powder. In the early experiments a narrow paper collar was slipped around the boss, and the cylindrical box made in this way on top of the piston was filled with the powder. In many cases, however, this led to mechanical instability resulting in detonations, as will be described in detail later, and in my recent work the material has been independently formed into a disc by compressing it in a mold in an arbor press to a pressure of 15000–20000 kg/cm^2. Most substances can be formed in this way into a disc coherent enough to handle, which is then slipped into the box formed by the paper collar. Quite recently, however, the paper collar has been entirely dispensed with, and it has been found possible to make the assembly by merely laying the disc on the piston, holding it in place by friction by pushing the piston against the anvil and holding with a screw of the assembly jig, and then repeating with the other piston. It is important not to get the thickness of the disc too great; 0.025 cm or less is a satisfactory value for most substances.

Qualitative Discussion of Nature of Phenomena

When pressure is applied the material of the disc flows out plastically between piston and anvil until an equilibrium thickness is reached, determined by the plasticity of the material. The distribution of stress in the material of the disc is evidently complicated. At the outer edge the stress component corresponding to the free face must vanish, whereas the stress component corresponding to the force exerted by the piston has the value of the stress in the steel. Toward the center it is reasonable to expect that a condition of local hydrostatic pressure is approached. It must also be considered that the surfaces of piston and anvil no longer remain flat; the distribution of stress in the disc will evidently depend importantly on the manner of distribution of stress in the steel. A complete solution of the problem would demand a knowledge of the properties of materials under the very high stresses operative here, and probably would also demand an extension of the mathematical theory of elasticity, because

doubtless Hooke's law no longer holds. Until such an exact solution has been obtained we shall have to content ourselves with mean values and with conclusions which are more qualitative in character than could be wished. It is possible, however, to obtain a few indications of the direction in which the actual values depart from the mean values.

The distortion of the anvil may be idealized as the distortion of a semi-infinite solid subjected to a normal pressure distributed over a circular area on its surface. The solution of this problem in elasticity theory has been obtained by Hertz, and may be found discussed, for example, on page 190 of the second edition of Love. If P represents the intensity of normal pressure in the stressed area of the solid, then the normal component of displacement, w, at any point of the surface of the semi-infinite solid is $\frac{\lambda + 2\mu}{4\pi\mu(\lambda + \mu)}\varphi$, where λ and μ are the familiar elastic constants, and φ is the ordinary electrostatic potential of a distribution of charge of surface density P on the affected area. Let us compare the normal displacement at the center and the periphery of the area of compression. Call "a" the radius of the area; denote values at the center by the subscript naught and values at the periphery by the subscript a. Then a simple integration gives at once:

$$\left.\begin{aligned} \varphi_0 &= 2\pi a P \\ \varphi_a &= 4\pi a P \end{aligned}\right\}$$

for the case where the pressure is distributed uniformly. Now compute numerical values for a mean pressure of 50000 kg/cm^2. $= 5 \times 10^{10}$ dynes cm^2. In Abs. C. G. S., $\lambda = 9.4 \times 10^{11}$ and $\mu = 7.7 \times 10^{11}$. The value of a for the apparatus was 0.32 cm. This gives:

$$w_0 = 1.50 \times 10^{-2} \text{ cm}, \qquad w_a = 0.96 \times 10^{-2} \text{ cm}.$$

That is, the center of the circle is depressed by 0.0054 cm more than the periphery. Doubling this difference to allow for the distortion of the piston, it appears that if pressure is uniformly distributed across piston and anvil the disc will be lens shaped, and 0.011 cm thicker at the center than at the edge. This roughly corresponds to the actual results. The disc in all cases was found to be lens shaped; the edge was usually very thin, 0.002 cm or less, and the center in a number of cases was 0.010 cm thick.

To a very rough approximation the material under investigation may be thought of as occupying a central chamber surrounded by a narrow channel through which it is being squeezed out, the friction

on the faces of the annulus holding in check the expulsive tendency of the approximately hydrostatic pressure in the chamber. With the actual dimensions of apparatus the annulus need not be very wide to hold the pressure in check. If dr is the width of the annulus, and h the thickness of the issuing film, then we have approximately $2\mu Pdr = Ph$, where μ is the effective coefficient of friction. Or $dr = h/2\mu$. Putting $h = 0.002$ cm, and $\mu = 0.01$ or more, this gives $dr = 0.01$ cm or less. The total radius is 0.32 cm, so that the confining annulus at the edge need have a width of only 3% or less of the total radius. In most cases this very crude approximation is probably significantly close to the actual state of affairs, judging by the appearance of the disc and other bits of evidence. To the next degree of approximation it is probable that the pressure at the center of the disc is not as great as at some distance from the center, the greater yielding of the central parts of piston and anvil under a uniform distribution of stress resulting in a lower pressure at these places of lesser effective stiffness. This means that in the ordinary substance the effective normal pressure at first increases from the periphery toward the center and then decreases again near the center. There must in any event be regions in the disc which are subjected to a pressure greater than the mean, that is, greater than 50000 kg/cm^2, but I believe that in the majority of cases the assumption of a mean pressure is not very far wrong. There are a few substances for which the pressure at the center appears to be significantly higher than the mean. Some substances apparently get trapped in the center and are not able to flow away laterally, for sometimes a little button has been found at the center on the conclusion of the experiment, much thicker than normal, with deep permanent central depressions in both piston and anvil, indicating a local intensity of stress much higher than normal. One may suspect that this sort of thing occurs when the stress of plastic flow increases very rapidly with hydrostatic pressure.

Assuming now a uniform distribution of normal stress under the piston, the mean coefficient of friction between material and piston or anvil may be computed from the turning moment of the force required to rotate the anvil. Putting this moment equal M, we have:

$$M = \int_0^a \mu Pr\, 2\pi r dr, \text{ or } \mu = \frac{3}{2\pi}\,\frac{M}{a^3 P}. \qquad \text{I.}$$

This equation may be taken to hold in the initial stages at low pressures when rotation is accompanied by surface slip. When friction becomes high enough, surface slip ceases, and plastic flow in the

interior begins. This matter will be discussed in greater detail later. If we assume that the shearing force, S, which accompanies plastic flow, is constant across the radius, the turning moment is now given by:

$$M = \int_0^a Sr.\, 2\pi r dr, \text{ or } S = \frac{3}{2\pi a^3} M. \qquad \text{II.}$$

The values given by these formulas for μ and S are probably lower limits in view of the fact that the pressure at first increases from the edge toward the center, the locality of greatest radius not coinciding with the locality of greatest force. An estimate may be made of the error arising from neglect of the variation of pressure by assuming that the pressure is a linear function of the radius, dropping at the periphery to one half its value at the center. A simple calculation shows that the coefficient assuming constancy is 15/16 of the true coefficient. Actually the variation of pressure cannot be as large as this, because if it were, more differential permanent distortion at the center of piston and anvil would be expected. Similar considerations apply to the shearing force. The assumption of a mean distribution of pressure probably introduces no important error.

The experimental procedure in making a run was as follows. The apparatus was set up in the way already indicated. A "seasoning" application of pressure was then made; the seasoning pressure might vary in magnitude from 5000 to 20000 kg/cm², depending on the nature of the material. For the softest materials it was only 5000 kg/cm², for the hardest materials 20000, and for most inorganic compounds 10000. At the seasoning pressure the anvil was rotated back and forth by hand through an angle of approximately 60° until the turning moment reached a steady value. In the majority of cases perhaps 20 double rotations were necessary. After reaching the steady state half a dozen more rotations were added for good measure. The seasoning was in practically every case accompanied by an increase in the turning force. An increase by 50% was not uncommon, and in extreme cases, when the original material had been in the form of a single crystal, the increase might be by a factor of 15. During the seasoning rotation the discs become continually thinner. In the case of metals the excess material was extruded in the form of a sheet into the free space between piston and anvil. It was necessary to continually operate the hand pump of the hydraulic press to take up the corresponding motion of the piston. The mere fact that plastic flow and extrusion takes place when the anvil is rotated but does not occur when the anvil is stationary, is itself of some significance as

showing that plastic flow in one direction is effective in making possible a plastic flow in a direction at right angles which would otherwise be inhibited by something analagous to friction.

After seasoning had been completed, pressure was released to zero and the regular run made. This consists in determining the force required to produce rotation at regular increments of pressure up to the maximum. The intervals were almost always 2000 kg/cm^2 and the maximum pressure 50000. Readings with decreasing pressure were also made in many cases, but not always. The rotating force at any definite pressure was taken to be the mean of the force required to maintain rotation in the two directions. The force recorded for either direction was the steady value of the force for that direction. When starting rotation in one direction after a change of pressure, or on reversal of direction of rotation, the force did not at once assume the final value, but might approach its final value in various ways, either dropping from a higher initial value, or climbing from a lower initial value, or in some cases passing through a more complicated pattern of variation, such as dropping and then climbing part way back to the initial value. The interval required to attain a steady value seldom extended over as much as 20°, the force during the final 40° of rotation being approximately constant. The force required to maintain rotation was in all cases nearly independent of the speed of rotation within the limits of convenient manual operation, which might be on the average 60° in 5 seconds. There are some substances, however, which do show a significant variation of rotating force with speed; these will be discussed later.

The character of the rotation varied widely from substance to substance. For 65 per cent of the substances it was perfectly smooth and quiet, but for the other 35 per cent rotation was accompanied by some sort of disturbance, which might be of the most varied kind. Deviations from smoothness could be both felt and heard; the audible effects were perhaps the most varied. The noise might be continuous, or have the character of a squeak or a grinding, and in one case there was a definite hissing. Discontinous effects might begin with a chattering (more often felt than heard), which might have a soft almost velvety feel to the hand, or which might become harsher and more abruptly punctuated, transforming into a snapping accompanied in extreme cases by jumping of the gauge on which the force was read of such magnitude as to make the readings uncertain. The usual order of events was for the disturbance to become more violent at the higher pressures, perhaps a soft chattering at very low pressures

changing gradually into a violent snapping toward the maximum, but this was by no means universally the case, and there are many examples of disturbances at the lower pressures which entirely disappear at the higher pressures. In most cases the disturbance was not great enough to introduce serious uncertainty into the readings. In case of a chatter the mean force was usually recorded; in case of a permanent snapping the maximum force just before the snap was more usually used. In a small number of cases there was a definite dependence of the disturbance on the speed of rotation, snapping or chattering at a higher speed disappearing at lower speeds. The readings were naturally made at the lower speeds. The force at such a lower speed might be markedly higher than at the higher speed, the substance chattering at a comparatively low force at the higher speed and rotating smoothly under higher force at the lower speed.

After completion of the readings, the apparatus was dismounted, notable features of the appearance of the residue and of pistons and anvil were recorded, and the mean rotating force plotted as a function of mean pressure. This curve of rotating force (or torque) against pressure constitutes the main results of the measurements, and the nature of the curve now requires discussion. At the low pressure end of the curve, rotation of the anvil is permitted, as already stated, by slip at the surface between steel and substance, as in ordinary experiments to determine sliding friction; the mean coefficient of friction can be calculated by equation I. If ordinary cylindrical coordinates are taken in the disc, r, θ, z, where z is the axis of rotation perpendicular to the face of the disc, then the stress component $\widehat{\theta z}$ in the interior of the disc is equal in magnitude to the tangential force at the surface exerted by friction. But now there is an upper limit to the shearing stress which any material can support, plastic flow being produced when this stress is reached. This stress is, of course, not sharply defined; it is modified by such phenomena as "work hardening," and may vary over wide limits. But work hardening cannot progress beyond a certain maximum, and there must be a shearing stress beyond which the body flows plastically no matter what its previous history. When the tangential surface force reaches this value, surface slip ceases, and flow by slipping on some shear plane in the interior of the disc begins. The piston and anvil are effectively one piece with the sheared specimen above this pressure. From this pressure on, the curve of rotating force against pressure refers to internal shearing flow, and the shearing stress at which such flow occurs, that is, the maximum shearing stress of the material, can be

calculated as a function of mean pressure by equation II. It is to be expected that the transition from surface slip to internal slip would be marked by some change in the character of the curve. Elementary considerations show the nature of such a change of character. In the range of ordinary pressure, the coefficient of friction has been found to be constant, independent of normal pressure, so that in this range, that is, in the initial stages, the curve should be a straight line passing through the origin. With regard to plastic flow, there are experiments in the range of stress encountered in engineering practice, for example

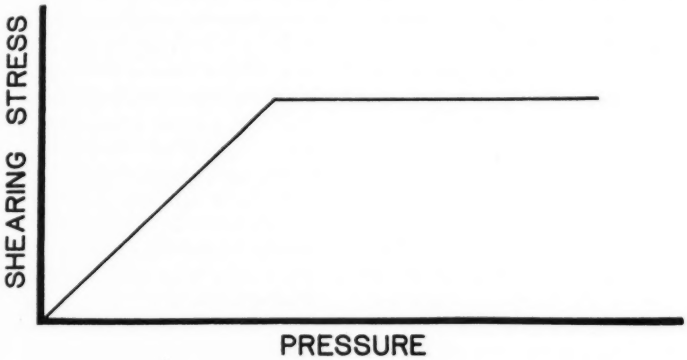

FIGURE 2. Idealized curve for substance with a plastic flow stress independent of normal pressure.

the experiments of von Karman, which show that the shearing stress at which flow occurs is approximately independent of the mean hydrostatic pressure. When the point of internal flow has been reached, the rotating force should correspondingly assume a constant value, independent of normal pressure, and the curve should consist of two straight lines, as in Figure 2. Very roughly this is the shape of most of the curves; that is, the curves are concave toward the pressure axis, but the deviations are very considerable, and give important information about the properties of the material as a function of pressure.

The initial part of nearly all the curves is not straight, but is gently concave upward, that is, the equivalent coefficient of friction increases somewhat with increasing pressure. Such an increase is to be expected because of permanent changes in the character of the surface. It is well known that excessive friction in bearings results in one metal

seizing the other, that is, in an actual union of the two surfaces. At such points of union the coefficient of friction is infinite. Welding of the sheared metal to piston and anvil has been observed a great many times, particularly with the softer metals, so that this factor must be present in increasing the effective coefficient of friction. The numerical value of the coefficient in the initial stages of slip is not nearly as high as perhaps one might be prepared to expect. The well known experiments of Hardy[3] have shown that friction between perfectly clean surfaces may rise to values considerably higher than unity, and one might perhaps expect that these values would be approximated here because of the very severe surface deformation, which would be favorable to perfect contact. The coefficients actually found, however, were sometimes lower than 0.1, and very seldom indeed rose as high as 0.3. That is, the values under pressure were of the same magnitude as encountered under ordinary conditions without precautions to secure unusual cleanliness of the surfaces. The surface film, perhaps of adsorbed gas or of moisture or of oxide, must be responsible. The reason that the film is not broken through by the very severe deformation is that it has no place to go. However, there are certain effects which are probably due to a gradual incorporation of the surface film into the body of the metal. On release of pressure the lower part of the curve in practically all cases lies notably above the corresponding part of the curve with increasing pressure. This would indicate a partial breaking up of the film and seizing as a result of the excursion to the maximum pressure. The same phenomenon is shown after seasoning. In spite of the fact that seasoning was always continued until a steady value of the force was reached, in practically all cases the force when the same pressure was reached the second time in the course of the regular run was somewhat higher than during seasoning. This again is probably to be explained by some permanent diminution of the effectiveness of the film.

It would evidently be desirable to study much more elaborately the initial stages of the curve. In particular, experiments should be made in high vacuum in which the surface film has been entirely removed. In the absence of such experiments, which would demand an independent investigation by themselves, it is not obvious just what significance can be attached to the initial parts of the curves found in the following experiments.

The transition from the initial stage of surface slip to the final stage of internal flow is marked on the actual curves in the manner qualitatively suggested by Figure 3, that is, surface slip is terminated

by a "knee" in the curve, beyond which the curve rises distinctly less rapidly than in the initial stages, and usually with concavity toward the pressure axis. The curve practically never becomes horizontal beyond the knee, and the extent of its failure to do so measures the extent of the failure of the ordinary engineering assumption that maximum shearing stress is independent of mean pressure. The failure is very considerable indeed, and the very strong dependence of shearing strength on mean pressure is one of the important results

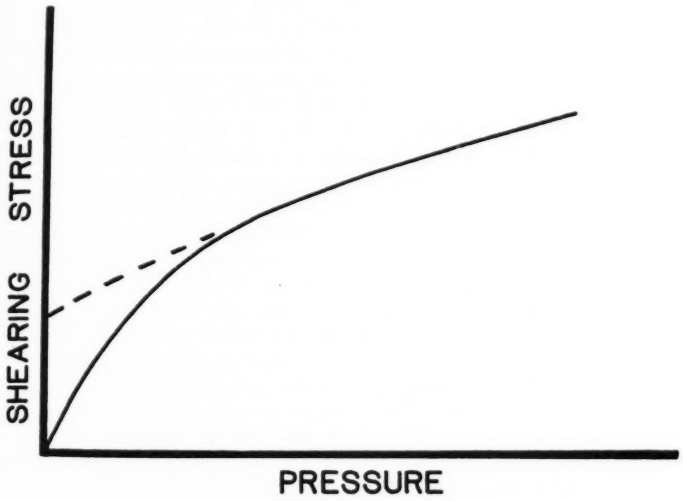

FIGURE 3. Typical shearing curve for the majority of substances.

of this investigation. This point has been considered in some detail in the two previous papers, and a table is given in the Physical Review paper for the effect of pressure. The increase of shearing strength is ordinarily by a factor of a number of fold for 50000 kg/cm^2.

The most common type of curve found experimentally is shown in Figure 3. The knee is never sharp, but is always more or less rounded, as would be expected from the fact that pressure is not truly constant over the entire area of contact. Beyond the knee the curve is descriptive of conditions inside the metal, rather than of conditions in the surface. For the average substance the knee occurs very roughly in the neighborhood of 20000 kg/cm^2. A rough extrapolation can be

made to indicate the internal conditions in the pressure range under the knee. At atmospheric pressure the maximum shearing strength is one half the tensile strength, and this is known for a number of materials. For some other substances the maximum shearing strength at atmospheric pressure can be found from the crushing strength. If this value is plotted on the axis of ordinates at atmospheric pressure, the curve above the knee can be roughly extended so as to cut the axis at this point, thus roughly giving shearing strength as a function of pressure over the entire range. The shearing strength found in this way is a lower limit to the actual shearing strength. This is partly a result of the pressure not being uniform across the disc, as already discussed, and doubtless partly the effect of the surface film. If this film is weaker than the bulk of the material plastic flow will take place in the film. If, on the other hand, the film is stronger than the bulk, then flow will take place somewhere in the actual material itself. This latter is more probably the proper alternative, because it is usual experience that a mixture of different sorts of atoms has a higher plastic yield stress than a pure substance.

The knee in the curve often marks a change in the character of the rotation for those substances which do not yield quietly or smoothly over the entire range. A common type is for the rotation to be smooth at low pressures, but to be accompanied by snapping or other disturbance at the higher pressures. In such cases the transition from quiet to noisy rotation often takes place at the knee. The interpretation is obvious. The noise arises from internal slipping, and this does not occur until the knee is reached. The converse state of affairs is also found not uncommonly, that is, noisy rotation below the knee, which becomes smooth above the knee. Here the interpretation is that surface slip is not a smooth phenomenon, perhaps involving continual seizure and rupture of the seized areas, whereas above the knee, where the surfaces are frozen into contact and this process ceases, internal slippage may take place smoothly. Or there may be disturbance both above and below the knee, which marks merely a change in the character of the disturbance; perhaps below the knee there may be squeaking and above the knee chattering. The frequency with which an alteration in the character of the rotation has been found associated with the knee confirms the interpretation of the knee as marking the change from surface to internal slip.

There are many other types of curve than the simple one shown in Figure 3, although this is by far the most common. Curves are not uncommon which beyond the knee eventually become convex

toward the pressure axis instead of concave like the type. Such a curve merely means that the shearing strength increases with pressure at an unusually high rate. An extreme example is afforded by paraffin, which is convex toward the pressure axis over the entire range. Paraffin is so weak under normal conditions and internal slip so easy that the knee must be at pressures below the possibility of observation with this apparatus. The entire curve therefore gives shearing strength as a function of pressure, which is seen to increase more rapidly than pressure itself.

A large number of curves have breaks of one kind or another, and the interpretation of these breaks now concerns us. Most of these breaks doubtless mean a polymorphic transition of the material. In general, one would expect the shearing strength of two different modifications, which of course have different crystal lattices, to be different, and therefore one would also expect a change in the curve of shearing strength on passing from one modification to the other. Under ideal conditions such a transition should be accompanied by a discontinuity in the shearing force itself, but because the pressure is not uniform over the disc, the transition is spread over an interval of mean pressure, and the expected break is usually smeared out into a more or less sharp change in direction. A few instances have been found, however, notably bismuth and tellurium, in which the break is sharp enough to give an apparent discontinuity when readings are made at pressure intervals of 2000 kg/cm^2. If the high pressure modification has the greater shearing strength, then the curve will rise more rapidly at higher pressures, giving a curve like that of Figure 4. A sharp upward break like this may be taken almost invariably to mean a transition. On the other hand, if the high pressure modification has the lower shearing strength, then the curve will rise less rapidly beyond the transition, giving a break which may be difficult to distinguish from the normal knee. There are plenty of examples of both sorts of transition, with of course all sorts of intermediate cases in which the difference of shearing strength of the two modifications may be too small to appreciably affect the curve.

This method of locating transitions from breaks in the shearing curve has the advantage of being rapid, since it is possible to determine a complete curve in about one hour. The shearing curves of the some 250 inorganic compounds to be presently described were determined mostly for this reason rather than because of any intrinsic interest in the shearing phenomena themselves. Up to the present, therefore, this shearing method has been used mainly as a tool in the

location of polymorphic transitions, and other results have been more or less incidental. The actual measurements on the transition were made in another apparatus permitting measurements of the change of volume and determination of the pressure of the transition

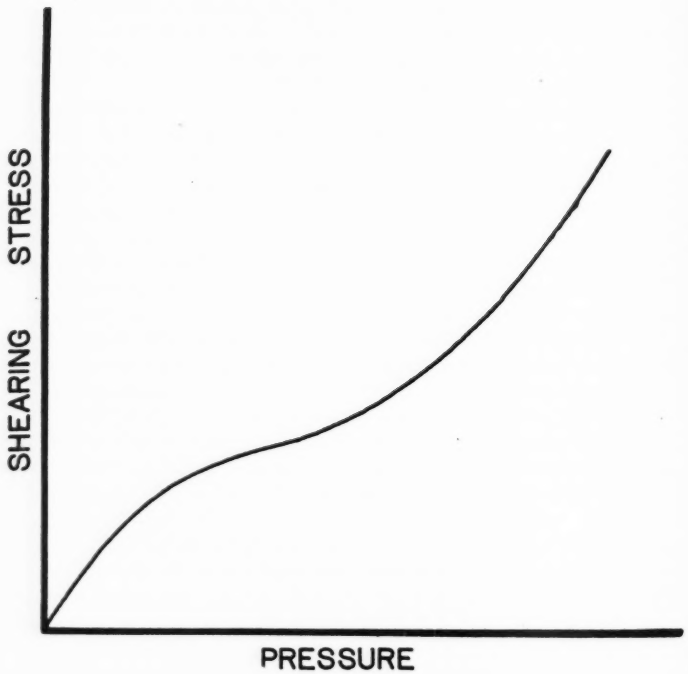

FIGURE 4. A common type of shearing curve for substances with a polymorphic transition.

as a function of temperature over a considerable range. The two methods—shearing and volume discontinuity—supplement one another in studying transitions. Thus transitions which do not show themselves by the shearing method at all may be obviously present when the volume apparatus is used, and conversely breaks have been found with the volume apparatus which correspond to nothing measur-

able with the volume apparatus. There is of course no reason why there should not be transitions with very small volume changes or with very small change of shearing strength, and such transitions would escape detection by one or the other or perhaps both methods. In detail, sixty-eight substances have been examined by both methods, of these thirty-three had shearing curves which justified the expectation of a transition, and among these twenty-five transitions were found by the volume method. Twenty-three of the sixty-eight had shearing curves indicating no transition, and only two transitions were found among these with the volume apparatus. The remaining ten cases were doubtful from the point of view of the shearing curves, and among these there were six cases of no transition and four of transition with the volume apparatus.

The method of exploring for transitions by determining the shearing curve is therefore one which has a fairly high expectation of success. The degree of success is even higher than indicated by the figures just given because of one interesting property of the shearing method. It is well known that phase changes often do not occur under ordinary circumstances which are favorable as far as the necessary conditions go which are expressed by the thermodynamic potentials. Thus many liquids may be subcooled into the domain of stability of the solid, or one solid modification may be superheated into the domain of stability of another solid modification. The usual explanation is that the appearance of a nucleus of the new phase, which is necessary to initiate the transition, and which is a statistical phenomenon, is inhibited by internal viscosity. It is natural to expect that the extreme distortion brought about by shearing would afford better opportunity for the formation of the nucleus of the new phase than would be presented by simple volume compression. This does in fact appear to be the case, and examples have been found of transitions by the shearing method at room temperature which could be found by the volume method only at a temperature a hundred degrees higher. As temperature falls the transition in the volume apparatus runs more and more sluggishly until at room temperature it becomes hopelessly slow. Several of the substances for which transitions were anticipated from the shearing curves but for which the volume apparatus showed none had rather high melting points; it is to be expected that in these cases the transition could be found with the volume apparatus at a temperature nearer the melting point.

If irreversible changes take place in the substance under shearing stress, breaks in the curve are to be expected which might be inter-

preted as transitions. Several of the unsuccessful predictions are doubtless to be explained by this effect. This matter of irreversible change will be discussed in greater detail presently.

The mean pressure at which a transition occurs with the shearing apparatus is usually somewhat displaced from the pressure at which it occurs in the volume apparatus. This is to be expected, because simple thermodynamic reasoning shows that the pressure of a transition is displaced by shearing stress acting at constant temperature. A number of years ago I derived a formula for the displacement of a transition by shearing stress.[4] The result is very simple:

$$\Delta\tau = \frac{\tau}{L}(W_1 - W_2).$$

$\Delta\tau$ is the displacement of the absolute temperature, τ, of equilibrium at constant pressure. The corresponding displacement of pressure at constant temperature can be found at once from Clapeyron's equation. L is the heat of transition in appropriate mechanical units, W_1 is the work done by the corresponding shearing stresses on the phase (1) stable at higher temperature, and similarly W_2 is the work of the shearing stress on the low temperature phase (2). The direction in which the temperature or pressure of transition is displaced by shearing stress therefore depends on the sign of $W_1 - W_2$, that is, on the relative elastic constants of the two phases. If we assume the normal state of affairs to be that in which the high temperature phase is more deformable, then W_1 will be greater than W_2 and the transition temperature will be raised at constant pressure, or the transition pressure depressed at constant temperature for a normal transition for which Δv is positive. It is to be noticed that within the region within which Hooke's law is valid the work of the shearing stress is proportional to the square of the stress, so that at higher shearing stresses large effects are to be expected. As a numerical example, consider a substance with a shearing strength of 10000 kg/cm^2, which is high for most substances, and let us suppose that the shearing deformation of the high temperature phase is 10^{-1} under this stress, that of the low temperature phase is half as much, the latent heat 1000 kg cm/gm (which is of the order of magnitude of that for many solid transitions) and $\tau = 300°$ Abs. Then $W_1 - W_2 = 250$, and $\Delta\tau = \frac{300}{1000} \times 250 = 75°$, so that very appreciable displacements are to be expected.

Another possibility to be kept in mind is that transitions may be

possible under shearing stress which will never occur under any combination whatever of simple pressure and temperature, so that novel phases may be called into existence by shear. For example, one could imagine a transition such that on the normal pressure-temperature plane the transition occurs everywhere at negative pressure, and is therefore unrealizable, but such that by sufficient shearing stress the transition line is displaced into the region of positive pressure. The unrealizable phase, normally stable only under high negative pressure, could under these conditions be produced at atmospheric pressure by the application of sufficient shearing stress. A possible, although not a certain example of such a transition has been found in lithium.

It is not uncommon to find breaks in the shearing curve before the knee has occurred, that is, in the region of surface slip, and which correspond to transitions found with the volume apparatus. This means that the ordinary coefficient of friction may also suffer a discontinuity on passing through a transition point. There is no reason why this should not be the case, and in fact it is to be expected, but as far as I know this phenomenon has not previously been studied.

It is obvious that a proper understanding of these shearing phenomena involves some sort of picture of the constitution of the material under such extreme deformations. One might be inclined perhaps to think that the material must be completely amorphous, with no trace of the original lattice structure. There is, however, one phenomenon which indicates that in at least some cases the lattice must still be present to an important extent. A polymorphic transition involves a change of lattice, and the fact that transitions can be located from their shearing curves means the existence of a lattice in blocks of sufficient size to impart physical properties to the block characteristic of the lattice. The probable size of these blocks must be a function of the material and of its capacity for recrystallization at room temperature. Some idea can be formed of the structure of the material after release of shearing stress and pressure by X-ray powder patterns. All degrees of distortion of the original lattice have been found in this way. Some substances show very little change in the character of their X-ray lines, but the lines of most substances are more diffuse after shearing, indicating a smaller size of the individual grains. The diffuseness may be so great as to entirely obliterate all trace of a pattern; such an effect has been found by Dr. Greninger in copper and indicates a grain size of perhaps not more than 10 atoms on a side or 1000 atoms per block.

Plastic flow itself must be accompanied or perhaps even made possible by the establishment of some sort of structure in the material. This is shown by the fact that whenever the direction of rotation is reversed, the force does not at once attain its steady value, but there is an interval of adjustment. The natural explanation is that during the adjustment the internal structure is being changed from that appropriate to one direction of rotation to that appropriate to the other. The adjustment process may be of at least two kinds. On reversal the force may be initially higher than normal and reach its steady value by dropping from above, or it may become steady by climbing from below. The phenomena are very complex; cases are not uncommon where the nature of the adjustment process changes with pressure, perhaps at low pressure the force climbing to a steady value, and at high pressures dropping to a steady value. It would be difficult to actually check by experiment any suggestion as to a possible mechanism to account for these effects, but it is obvious that a possible explanation is afforded by a reorientation of the crystal blocks in such a way that their internal slip planes become either more or less favorably situated. Analogously to certain of the well known theorems in mechanics one might perhaps expect some general proposition to apply to the phenomena here, such perhaps as that reorientation takes place in such a way as to bring into proper alignment the maximum number of slip planes. But there is no such general proposition as is shown by the existence of phenomena with both signs. The phenomena are obviously complex, for in general slip does not take place exclusively on one set of planes, but more than one set must be involved, and such different sets may have different intrinsic properties, and furthermore different net effects due to difference in number and geometrical arrangement in different substances. There does seem to be one general result, however, namely that orientation never takes place spontaneously in such a way as to allow slip to take place continuously on a single set of planes. If a slip plane were located parallel to the surface of the disc, obviously slip might continue to take place indefinitely on this plane. A number of experiments were tried in which the disc was initially a single crystal with the principal slip plane parallel to the surface of the disc. In such cases the original crystal structure is rapidly destroyed by the rotation, and the resistance to shear increases very rapidly. Examples are zinc, graphite, and mica.

The reorientation of the blocks may conceivably be brought about either mechanically by a reorientation of the crystal blocks as wholes,

or by recrystallization into the new orientation. Recrystallization must involve the formation of a new nucleus, and growth from this nucleus. Recrystallization might not be expected to be important at ordinary temperatures, but the mere fact that polymorphic transitions occur shows that sometimes it is possible, because such transitions must involve the appearance of a nucleus of the new phase and growth from the nucleus.

If the substance is capable of spontaneously recrystallizing one may expect an effect on the character of the plastic flow curves. The mobility possible during recrystallization is in certain respects similar to the mobility of an ordinary liquid, and one might perhaps expect that for such substances the rate of plastic flow would vary importantly with the deforming force. Although it is true that the speed of flow is approximately independent of the force for most substances, nevertheless there are some substances for which the speed varies greatly with the force. This is evidently an important effect, and a special study was therefore made of variations of speed with force which will now be described.

Measurements at Constant Force and at Constant Speed

For this study it was necessary to modify the apparatus since the usual manual operation did not permit a sufficiently wide range of variables nor a sufficiently accurate control. A sector of a circle of channel iron was rigidly attached to the rotating lever, with the center of the sector at the pistons. Motion was imparted to the lever by means of a light wire cable, so arranged as to wind or unwind itself upon the circular sector as rotation proceeded. This cable was carried over a fixed pulley, either to an adjustable weight, for the experiments at constant force, or else to a winch, for the measurements at constant speed. The winch was improvised from a back geared lathe head by reversing the connections of the gearing, as could be readily done. It was driven through the main spindle, and the cable wound itself up on the driving pulleys. The source of power was a three phase ¼ H.P. motor, with windings so connected as to reverse in direction on throwing a switch. Various gears and worm reductions between motor and winch allowed a wide range of speed; the range actually used in the experiments was 10000-fold. The power demanded was only a small fraction of the available ¼ H.P., so that there was no appreciable variation of speed of the motor for any variation of load. The rotating force was measured in the experiments at constant speed by inserting into the cable a very stiff helical spring, the stretch of

which was measured with an Ames dial gauge, the combination constituting a simple spring balance which operates with negligibly small deformation. Rotation in either direction was provided by the use of a counterweight and a second cable attached to the sector, the counterweight being heavy enough to drive the apparatus on reversal of the motor. The zero of the spring balance was set to correspond with the counterweight. The sector was provided with a scale

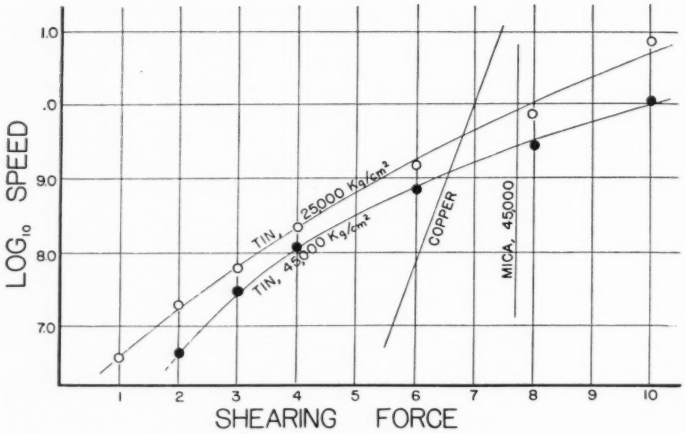

FIGURE 5. The relation between shearing force and speed of rotation at constant normal pressure for various substances. Both coordinates are in arbitrary units.

graduated to millimeters, and speeds were determined from the scale and a stop watch.

The experiments were by no means systematic or complete. There is an immense amount of routine work that could be done here with a great variety of materials; all that I have attempted is to get some idea of the qualitative phenomena possible with different substances. Measurements were made with tin, lead, copper, silver, mica, borax glass, SiO_2 glass, calcite, and graphite. Tin and lead show to the greatest extent the variation of speed with force. In Figure 5 is shown the logarithm of the speed of rotation of tin as a function of force. For a 10000 fold variation of speed there is a variation of force by a factor of approximately 10. This is still very far indeed from the behavior

of a viscous liquid, for which the speed would vary proportionally to the force, but it is also far from the behavior of the normal plastic solid, which has a speed nearly independent of the force. Figure 5 shows log speed as a function of force for two pressures, 25000 and 45000 kg/cm^2. The speed becomes less at the greater pressure, as one would expect, or in other words, the force at constant speed increases with pressure. There is also a recognizable change of shape of the curve at the low force end as pressure increases in such a direction as to suggest at higher pressures a sharper lower limit to the force required to produce rotation. That is, at 45000 one can specify more definitely the lower limit of the force below which rotation will not occur than one can at 25000. At atmospheric pressure it is of course known that slow creep of some metals persists for exceedingly low values of the force.

The phenomena with lead were qualitatively similar to those with tin, but the deviation was in a direction toward more normal metals. Thus for a two fold increase in the force the increase of speed for lead was by a factor ten fold greater than the factor for tin. Fewer measurements were made on copper and silver than on tin and lead, but the trend was in the same direction. The relation between speed and force (arbitrary units) for copper is shown also in Figure 5. Because of the arbitrary units the only significant feature about the curve for copper is its very much more rapid rise. That is, for a comparatively small range of force the range of speed is from something too small to measure to something too great to measure. For ordinary manual operation this would give the appearance of a force independent of the speed, which is normal. The results for these metals suggest the generalization that the higher the melting point the more nearly is force independent of speed. It also suggests itself that the mechanism of plastic flow for a low melting metal like tin may perhaps be mostly a recrystallization mechanism, the facility of recrystallization being largely determined by the proximity of the melting point. We have already seen that if flow is produced by recrystallization it would persist over a comparatively large range of force. The variation of the force-speed curve with pressure is also consistent with this picture. Roughly the effect of pressure on this curve (in addition to the displacement along the axis) is to make it steeper, that is, to alter it in the direction of the curves for higher melting metals. But the effect of pressure is to increase the melting point.

The mechanism of yield in a normal metal with high melting point,

for which the force is independent of the speed, on the other hand has obvious points of similarity to the ordinary frictional sliding of one surface on another.

A special study was made of the nature of the seasoning phenomena in lead, the measurements of rate at constant force providing an especially simple way of doing this. The speed of rotation produced by a constant force was found in one series of experiments to decrease continuously by a factor of 3 as the number of rotations through the regular double 60° increased from 1 to 100. Even after 100 rotations the speed was still decreasing perceptibly. This effect is in the direction to be expected, namely in the direction of a hardening produced by the continued deformation. If hardening regularly increases over such a long interval as this it means that the curves of shearing force against pressure obtained in the regular way do not refer to a final steady state, but are somewhat in error. Any such error, however, particularly for substances with a steeper curve of log speed against force, is too small to show on the scale usually employed. The existence of seasoning effects over such a wide range suggests the possibility of a greater range of internal structure than one would ordinarily expect, or a greater sensitiveness of shearing force to slight changes in such structure. One experiment with lead showed a paradoxical softening instead of the expected hardening, that is, an increase of speed instead of the expected decrease after a few rotations. However, the results were always somewhat capricious, and probably the number of rotations in this case was too small for significance.

Silver showed very marked hardening effects; after a seasoning by 50 double rotations the hardening during a single rotation was still so great that under constant force a very rapid initial rate of rotation had dropped to a barely perceptible creep in less than 60°. Obviously if the force is nearly independent of speed, as it is for silver, then measurements at constant force will be extraordinarily sensitive to a slight amount of hardening.

Measurements on copper were made over the entire pressure range to determine whether there was for it any significant variation with pressure of the effect of force on speed. No such variation was found within the limits of error of the measurements, which were somewhat irregular. Over the entire pressure range it required on the average an 8 per cent increase in the force to produce a 15-fold increase in the speed.

Mica shows phenomena considerably more complicated than the metals. Experiments made at constant force showed in the first

place a much smaller range of force within which the speed varied from too small to measure to too large to measure. Furthermore, the sharpness of the limits of force increases with increase of pressure. Thus at a mean pressure of 20000 barely perceptible creep began at a mean shearing stress of 8300 kg/cm^2, and at 10000 kg/cm^2 shearing stress the creep had become a running away of the lever. At a mean pressure of 40000 there was no perceptible creep at a shearing stress of 19,300 kg/cm^2, and at 19,700 it ran away. Notice incidentally that these shearing strengths are very high. In the range of measurable motion just below the force producing instability the phenomena were quite capricious; creep was not at all regular, but there might be creep for a while, then a little jump, then sticking for a while, until the cycle of creeping and jumping repeated itself. The final instability and running away happened in the same way; for the critical force there was at first slow creep and then after a few minutes the system suddenly became unstable and ran away. At the highest pressure 40000, however, no creep was observed before the instability, but it immediately ran away on increasing the stress from 19,300 to 19,700.

The runs at constant speed showed different phenomena. For speeds corresponding to that of ordinary manual operation there was in the first place a perceptible variation of force with speed, and in the second place the rotation was punctuated with frequent snapping. This snapping means an internal rupture of the mica; because the apparatus is not infinitely stiff this rupture is accompanied by elastic yielding in parts of the apparatus and a drop of the rotating force. As rotation proceeds after a snap force rapidly builds up again to its former value, rotation then proceeds quietly for a while at a constant force, until there is another snap, and the cycle repeats. One surmizes that the snapping of the constant speed experiments corresponds to the running away of the constant force experiments. At lower speeds of rotation, however, under 0.04 radians per minute, the snapping entirely ceases, and rotation through the entire 60° is accomplished quietly.

It would seem that two phenomena coexist here. Mica has the capacity for continuous smooth plastic flow, but if the speed of deformation becomes too high, then the second phenomenon of rupture appears. This, as I have already emphasized in my geological paper, I believe to be of considerable significance for geology. What the exact mechanism of rupture is cannot at present be stated. It must be that plastic flow is accompanied by some process of spontaneous

internal readjustment, which proceeds at a characteristic speed. If the speed of deformation is so great that the spontaneous readjustment cannot keep the body in such a condition that it is adapted to flow, then it breaks. Whatever this process of internal adjustment is, it need not necessarily be accompanied by any important rise in the shearing strength; in the above experiments after each snap the force rapidly climbed back to its normal value and remained there without a sensible change until the next snap occurred.

If the pressure is varied at constant speed of rotation of the mica, the snapping is found to become rapidly more frequent as pressure increases.

After the termination of a run with mica, the crystal structure was found entirely destroyed, and little more was left than an impalpable powder. This powder sticks very tightly to the steel and has to be scraped off. The original grinding marks on the steel are not touched, showing that mica has not become harder than steel under pressure.

Borax glass was studied only with the apparatus for constant speed. This shows the phenomena of snapping like mica. The snapping also increases in frequency with the speed of rotation; thus at a speed of 0.009 radians per minute snaps occurred at the rate of 8 per radian, and at a speed of 0.5 radians per minute there were 28 snaps per radian. I did not find a speed of rotation so low that snapping entirely ceased, although such had been found for mica. There is also an important effect on reversing the direction of rotation; the snapping does not begin on reversal of direction until a much greater angle has been passed over than the normal distance between snaps. This seems to be definite evidence of some sort of internal structure depending on the direction of plastic flow. It is interesting that borax glass, which is non-crystalline, should show the effect so prominently. The effect of pressure on the rupture of borax glass is strikingly different from that on mica, for in borax glass the angular interval between snaps becomes markedly less as pressure increases instead of greater.

After completion of the shearing runs the borax glass was found completely self-welded into a homogeneous mass, which also stuck to the steel and apparently wet it around the edges like the familiar fused borax bead. Determination of density by the flotation method showed no perceptible permanent change of density. The glass therefore probably does not crystallize under these conditions.

Quartz glass at the maximum pressure (50000 kg/cm^2) in the apparatus for constant velocity showed only phenomena of snapping

(rupture) without any trace of plastic flow. That is, after each snap, the force rapidly built up again, and as soon as the previous maximum was reached, with no interval of yield, rupture again occurred at once. Motion during running away was accompanied by continual cracking, whereas the running away of mica was quiet. An increase of density was found by the flotation method, but this may have been due to fragments of steel rubbed off the piston, visible after the run as a gray surface streak. Dr. Greninger made an X-ray analysis and found faint lines of α-Crystobalite, but since he has found evidence of the same lines in ordinary quartz glass, the evidence is uncertain for any crystallization produced by the shearing. Finally graphite, in the form of massive Acheson graphite of commerce filed to a powder, was tried, mixed with a very small quantity of diamond dust of the kind used in polishing. The object of the diamond dust was to act as a possible nucleus for the transformation to diamond. There was no trace of transformation. Seasoning was performed by hand; rotation was at first perfectly smooth and easy, but after a few rotations surprisingly high resistance developed and there was now much snapping. Examination at constant speed (0.0036 radians per minute) at 50000 kg/cm^2 showed only the phenomena of rupture, with no trace of creep, just as had quartz glass. It was a surprise to find no trace left of the internal slip of graphite which under ordinary conditions is so prominent as to give it its chief commercial importance.

Resistance Measurements

Significant information about the condition of the sheared film may be expected from measurements of the resistance of the film as a function of pressure. One could not expect to get the pressure coefficient of resistance of the material of the disc because of too great uncertainty arising from the indeterminate geometrical shape, but I anticipated that information could be obtained as to whether the material had experienced a transition, and the first use contemplated for this method was in establishing the existence of transitions which perhaps had been made probable by the measurements of shearing force, but which had too small a change of volume to register in the volume apparatus.

The method was a potentiometer method. Current was led in at one piston, which was electrically connected with the piston of the hydraulic press, across one disc, across the anvil, across the other disc to the second piston, which was insulated from the lower platen of the press by a thin sheet of mica so large in area that the mean

stress in it was not important, and back to the rest of the circuit. Potential taps were made around each piston and the anvil, so that the potential could be measured around each sample. A high sensitivity galvanometer was used for the measurement of potential. Measurements were first made on bismuth. A preliminary calculation had indicated the order of magnitude, and it was a very great surprise to find the resistance 2500 times greater than had been anticipated. The actual resistance was 0.005 ohm. It must be remembered that the thickness of the film is only 0.005 cm., so that the resistance to be expected is very small. A great deal of time was spent in trying to straighten out the discrepancy in order of magnitude. As far as I could find very little work has been done on the resistance at the point of contact of two pieces of metal pressed together mechanically. I made measurements with other metals as blanks, and even took the precaution to make up out of a single piece of steel a conductor of the same geometrical shape as pistons and anvil in order to eliminate any possible geometrical effect. There is of course a contribution to the total resistance made by the spreading of the lines of flow through narrow necks which can be approximately calculated and which turns out to be of the same order of magnitude as the contribution made by the cylindrical flow in the short bosses of the pistons. But all such contributions to resistance were 100 times smaller than the actual discrepancy, so that the discrepancy of 2500 fold remains. At one time I entertained the notion that there might actually be a resistance of this magnitude at the interface arising from a transition zone in which the electronic wave functions suitable to the interior of one metal change to the wave functions suitable to the interior of the other. Apparently the magnitude of such transition effects has not been calculated, so that there was conceivably a possibility of explanation here. But this was ruled out by an experiment in which contact was made by fusing bismuth directly to copper; the resistance in the transition zone was found to be of the order of 1000 times less than in the shearing experiments. In the end there seemed to be no alternative but to accept the high value of the resistance as actually true, and to explain it as the effect of impurities in the surface layer, due perhaps to gas or moisture or oxide originally absorbed on the surfaces of piston and anvil or specimen. One reason that I was slow in coming to this point of view was that the properties demanded of this surface film in order to explain the results are different from those anticipated. If the resistance of the film is plotted as a function of pressure the regions of polymorphic transition are marked by large

drops in the resistance. This is shown in Figure 6 where the first step, at which resistance drops by a factor of 2.5, corresponds to the transi-

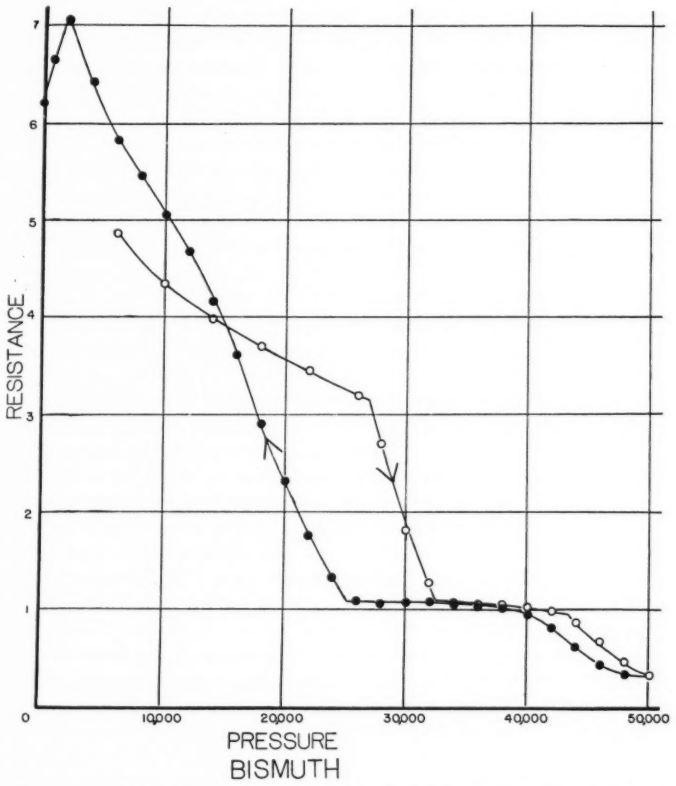

FIGURE 6. The electrical resistance in arbitrary units of a thin film of bismuth between piston and anvil.

tions I–II and II–III, which are too close to be resolved, and the step at the upper end of the pressure range, where the resistance drops by a factor of 3, to the transition III–IV. Of course breaks in the resistance at a transition were just what was expected, but the surprising thing is that the absolute magnitude of the resistance, even through

the breaks, is hundreds of times greater than that corresponding to the resistance of the pure metal, so that the breaks must be contributed by the impure surface films. That is, the surface layer has a resistance of the order of a thousand times greater than pure metal of the same thickness, due to disorganization by the impurities incorporated in it, but nevertheless this surface layer has a lattice structure, characteristic of the phase, so interwoven with the impurities that when the lattice changes the resistance changes also. The surprising thing is that a lattice so disorganized as to have a resistance a thousand times normal can nevertheless go through changes corresponding to polymorphic transitions and thereby change the resistance by a factor of several fold. It would seem to be necessary to assume that the impurities initially on the surface have been incorporated by the drastic deformation into a layer at least a good many atoms thick on the surface of the pure metal.

It is evidently impossible when the situation is so completely dominated by the surface layer to extract any information about the resistance of the pure metal from these measurements. Actually the resistance of pure bismuth increases under hydrostatic pressure, whereas in the shearing experiments the resistance decreases with increase of pressure over the entire range except for the very last step with decreasing pressure. One cannot even be perfectly certain that the resistance of the pure metal decreases during the polymorphic transitions, but the great probability is that it does, because in every other known case the resistance at a polymorphic transition follows the change of volume. Evidently experiments would be extremely desirable here in which the surfaces had been made initially clean by out-gassing in vacuum.

The experiment was at one time so arranged that the resistance could be measured during the actual rotation. No perceptible change of resistance took place during this operation either for bismuth or for several other metals, showing that the surface layer remains at least relatively intact during shearing.

Experiments were made on a number of other metals than bismuth. All of these showed an abnormally high resistance, but most of them by a very much smaller factor than the 2500 of bismuth. Evidently bismuth is abnormal with respect to the resistance of its surface layer as it is also with regard to so many other properties.

A blank run was made with the steel piston pushing directly against the steel anvil. The initial resistance, presumably due to the presence of surface layers, was of the order of five times that expected. It

required the full 50000 kg/cm² to reduce this resistance to the resistance of the dummy made of a single piece of metal. Silver shows a resistance of the surface layer somewhat greater than that of steel; above 40000 this resistance practically vanishes, leaving only the resistance of the steel parts.

Tellurium is a semi-metal with very high specific resistance, of the order of 0.4 ohm cm under normal conditions, and with the abnormal property that the addition of impurity decreases the resistance, bringing it into the direction of a normal metal. Corresponding to this, the total resistance between piston and anvil was that to be expected for the pure material, the surface layers, if there were such, now making a negligible contribution. Resistance is known to decrease strongly with increase of pressure, and in fact there was a large continuous decrease of resistance in the present apparatus up to 40000 kg/cm², at which there was a further discontinuous drop of resistance by a factor of 2.3, corresponding to the polymorphic transition in this vicinity already investigated. Under the circumstances there can be no doubt but that the specific resistance of tellurium actually decreases at the transition.

Thallium, like bismuth, is a metal which gave a resistance between piston and anvil very much higher than to be expected; in fact the discrepancy was by a factor of 4000, even higher than for bismuth. This probably is to be explained by the heavy coating of oxide which can be seen with the eye to form rapidly on a freshly scraped surface. The effective resistance was found to drop rapidly with increasing pressure, and at 40000 there was an additional more abrupt drop due to the transition already known and studied at this pressure. At the maximum pressure, beyond the transition, the resistance had dropped approximately to that of the steel parts, the contribution of the surface layer thus dropping out. At the transition, however, the surface layer still dominates, and the remarks made with respect to bismuth about the lattice change in the surface layer are applicable.

Thorium, a metal with high melting point and not appreciably oxidized under normal conditions, on the other hand shows no well defined surface layer phenomena, but the entire resistance was of the order of that contributed by the steel parts, which was several fold larger than the contribution of the pure thorium alone. There were indications, but not certain evidence, of a decrease of resistance on passing through the transition known from previous shearing measurements to probably occur in the neighborhood of 12000 kg/cm²; the relative resistances are too unfavorable to permit anything very

definite here. Thorium was unusual, however, in showing a permanent change of resistance on shearing. Measurements had been obtained lying on a fairly smooth curve up to 30000 with no rotation. Here rotation was first made and there was at once a permanent drop of resistance by about 25 per cent. From here on a fairly smooth curve was followed of the same general trend as the initial curve, and with no further effect of additional rotations. One may suspect some permanent change produced by the rotation in the comparatively unimportant surface layer.

Finally, a few measurements were made on substances normally insulating. The resistance of mica was measured. The discs were initially 0.005 cm thick. Pressure was applied at once to 50000 with no perceptible alteration in the perfect insulating properties. Shearing stress was then applied by the usual rotation. For the first few rotations there was no effect, but then a partial short circuit appeared, which opened and closed spasmodically during rotation, until after perhaps 20 rotations a steady value of the partial short circuit was reached at a value of the resistance many fold greater than for metals. There would seem to be no question but that mica retains its insulating properties under high pressure and during the deformation of shearing stress. The degree of conductivity actually observed is perhaps an effect of the small abraded particles of metal, or even the very close approach of piston and anvil around the edge of the piston. In a great many cases after the conclusion of a run an outline of the piston on the anvil is found in the form of a very narrow burnished line. It is not unreasonable to suppose that there is effective contact between the two steel parts along this line. The area of this region of contact must be very small, and there is no reason to think that it can introduce appreciable error into the measurements of shearing force.

Another insulating substance, Bi_2O_3, was selected for an entirely different reason from mica. Other lines of evidence, to be discussed presently, suggested very strongly that shearing deformation decomposes Bi_2O_3 to the pure metal. If pure metal were present, this should perhaps be disclosed by the resistance measurements. Pressure was applied up to 30000 with no change in the insulating properties. At the first touch of rotation at this pressure a short circuit developed, which persisted without interruption throughout many subsequent rotations and changes of pressure. At 50000 the resistance was found to be practically the same as had been found previously due to the steel parts alone. The explanation is doubtless

that there is partial reduction of Bi_2O_3 by the shearing force, and that bridges of metallic bismuth are built across between the two steel surfaces. The appearance of the sample also suggested this; the unaltered Bi_2O_3 was capriciously interspersed with a blackish substance filling the cracks and crevices.

Ag_2SO_4 is a substance with a remarkable shearing curve, the force being constant beyond a pressure of 15000 kg/cm², and a possible explanation is decomposition to the metal. At pressures up to 20000 the resistance was high, but this resistance could be very materially reduced by a few rotations. At higher pressures there was mostly a dead short circuit, which however, sometimes capriciously changed to a high resistance on rotation. The original high resistance was recovered on release of pressure. The phenomena are not inconsistent with the idea that there is some free silver present at the high pressures, but the results are too capricious to warrant much confidence with regard to this conclusion.

Finally, $HgSO_4$ was examined in much greater detail than the other insulators. The shearing curve of this has a very pronounced maximum, but no polymorphic transition could be found in the volume apparatus. Up to about 20000 the resistance is high; the resistance becomes higher during the actual rotation and then slowly recovers when rotation ceases. Between 20000 and 30000 the effects reverse; the initial resistance becomes rapidly less, and during rotation the resistance becomes still less, approaching a short circuit. Above 30000 there is practically continuous short circuit, with or without rotation. The pattern of behavior is roughly retraced on releasing pressure. Again the phenomena are not inconsistent with the presence of free metal at the high pressures and suggest that the appearance of free metal is facilitated by the shearing stress. Further study is necessary, however, before this conclusion can be regarded as certain.

Irreversible Phenomena

A number of different sorts of irreversible phenomena were encountered in these experiments, of varying degree of significance. In the first place, the curves of rotating force against pressure very seldom exactly retrace themselves on release of pressure. There appear to be several possible reasons for this, the exact reason not being always easy to find. The only obvious generalization with regard to the shape of the curves is that at the lower end of the curve the shearing force is always greater on release of pressure. The zero reading shows the maximum variation, and may be increased by as

much as four times by the excursion to 50000. This is not to be explained by friction in the press, because this would equally effect the initial zero reading, which was always made after a seasoning application of pressure. The explanation is doubtless an actual increase of friction due to an increased cohesion between the material and the steel, which in some cases becomes an actual welding. Permanent distortion of the steel parts is also doubtless sometimes a factor; sometimes at the maximum pressure a triangular ring shears off from the edge of the piston. This is always accompanied by a decrease in the rotating force, since the effective moment of the resisting force has become less because of the shorter effective radius. However, there were a great many cases of irreversible curves when no permanent change in the steel parts could be found. Doubtless by far the greater part of irreversibility is connected with the irreversible extrusion of the material of the disc itself. While pressure is increasing material is continually being extruded between piston and anvil, the disc thereby becoming thinner, whereas during decrease of pressure there is obviously no corresponding sucking of the material of the disc back toward the center. The precise way in which the material flows outward will involve the initial thickness and the way in which the shearing strength varies with the mean pressure. If it can flow out easily, then as pressure increases there will be a tendency for the outer parts of the disc to make a disproportionally large contribution to the total moment, resulting in a curve which rises too steeply. Sometimes, on the other hand, the material gets trapped at the center, the central part bears the brunt of the pressure on a little button which imbeds itself deeply into the steel, and the total turning moment is too small because of the small radius of this button which carries more than its share of the load.

The irreversibility is sometimes particularly striking when the curve has a break due to a polymorphic transition. A generalization can be made here, namely that the discontinuities are always more marked with increasing than with decreasing pressure. Figure 7 for NH_4ClO_4 shows a striking example of this. The explanation is probably that the application of shearing stress is accompanied to a certain extent by actual running of the transition during the duration of the stress. Plastic flow, in the region of the curve where the phases may coexist, is not to be thought of as taking place in a substance consisting of a definite fraction of one phase and a definite fraction of the other, but during plastic flow the transition is actually running, changing the relative amounts of the two phases. While the transi-

tion is running internal stresses have a chance to relieve themselves, the material is effectively more in the condition of a liquid, and flow will take place at a lower force than would otherwise be possible. During the transition the shearing force will be too low, and this will be the case in whichever direction the transition runs. Thus in

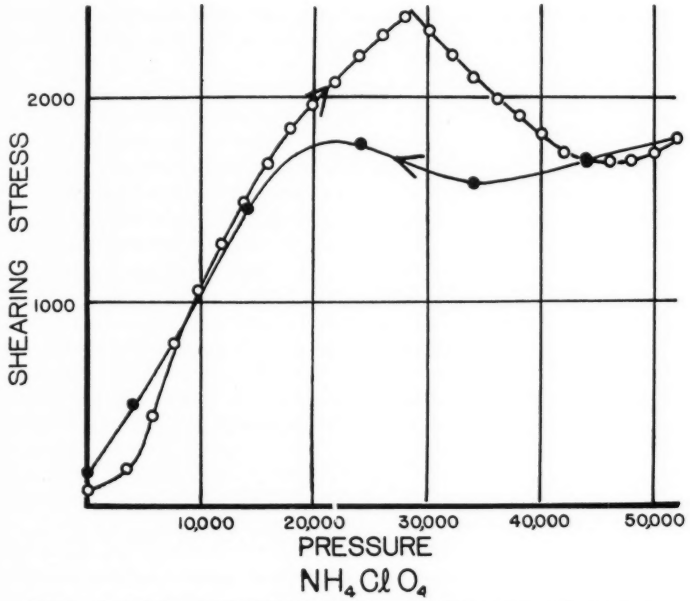

FIGURE 7. Shearing curve for NH_4ClO_4, showing that the breaks in the curve are usually more abrupt with increasing than with decreasing pressure. Both ordinates are in kg/cm².

Figure 7, during the transition zone from *A* to *B* with increasing pressure, the force is abnormally low, and the curve drops more than it otherwise would, whereas on release of pressure in the transition zone from *C* to *D* force is also too small, and the curve does not rise as much as it normally would. The result is that the curve with increasing pressure is much more likely to reveal the existence of a transition than that with falling pressure. Since the principal interest in the exploration of these substances was to discover the existence

of polymorphic transitions, in many cases readings with decreasing pressure were not made at all, and in many other cases they were made at wider pressure intervals than with increasing pressure. The elements, however, were examined consistently with both rising and falling pressure.

At present there seems to be no feasible method of calculating the precise effects of plastic flow on a transition. Because of the irreversibility in the plastic flow itself the methods of thermodynamics obviously do not apply.

There is one sort of irreversibility which played a prominent part in my early work on shearing. There were a large number of examples of denotation, with frequently accompanying chemical transformation. If a pressure of 50000 was applied at once to the material, it often happened that the first rotation was accompanied by a loud detonation, often with flashes of flame. It was my original idea that this was due to a chemical instability due to tearing apart of molecular bonds and the formation of new ones, but it now appears almost certain that chemical instability, when it occurs as apparently it often does, is at least only infrequently accompanied by detonation. The detonations were without doubt of mechanical origin. They are exhibited only when the initial thickness of the material is too great. Another aspect of the same phenomenon is doubtless the trapping of material at the center which is not infrequently observed. Sometimes the material, which is caught by friction, can escape when an additional mobility is provided by the rotation, and sometimes it cannot. Similar instabilities in the presence of frictional forces arise in other ways. Thus a number of years ago in attempting to form some of the harder and more brittle metals into wire by extrusion through a die I found rather frequently that the metal would completely resist extrusion up to a certain critical value of the extruding force, when it would suddenly let go, a mouthful of the metal would spit out, and the process would repeat.

I convinced myself that the detonations were in at least most cases of mechanical origin by experiments on celluloid. I had found that when celluloid is placed between pistons and anvil it detonates, without rotation, when a certain critical pressure between 20000 and 30000 kg/cm^2 was reached. There was a flash of flame and a residue of finely divided carbon. This of course was not surprising in view of the chemical relationship between celluloid and gun cotton. Chemical instability might plausibly be thought to result at a critical hydrostatic pressure combined with the shearing stress incidental to

the extrusion of the material. The clue to the matter was later found by varying the initial thickness of the celluloid; the pressure of detonation was approximately inversely proportional to the initial thickness. Obviously this cannot be a chemical instability at a critical hydrostatic pressure, but is more probably a mechanical instability. It is easy to see that the situation contains the possibility of mechanical instability. We have seen that to a very rough approximation the material of the disc can be thought of as consisting of an outer annular region in which the maximum shearing stress prevails, and an inner region in which the pressure is more nearly hydrostatic. When the total pressure is increased, the annular region creeps in toward the center. If it should ever happen that the annular region had reached the center, no further motion of the region is possible and instability must ensue, the disc not regaining its equilibrium until its thickness has been suitably reduced by extrusion. The work done by the high hydrostatic pressure acting through the displacement of the pistons accompanying the explosive extrusion puts enough energy into the system to produce local increases of temperature sufficient to bring about the chemical effects found with celluloid and a number of other substances. It is not by any means certain that there are not some cases of genuine chemical instability under shearing stress, but the subject lost its interest with the discovery of the effects with celluloid, and I have not pursued it further. Possibly the thermite reaction, which I have made to take place over a considerable range of initial thickness, is an example.

By far the most interesting irreversible phenomena are those of permanent chemical change of one sort or another. I have made no systematic examination of this matter, and the following results were obtained more or less incidentally. In general the subject is a very difficult one because of the very small amounts of material involved. The total amount of material subject to shearing stress is of the order of a few milligrams. This is small enough, but the difficulty is very much increased by the fact that in most cases the chemical alterations are apparently confined to the surface layer. In some cases enough of the material is transformed to allow definite evidence from X-ray analysis, but in a number of other cases there have been perfectly definite changes of color, showing obviously some sort of chemical change, for which no corresponding alteration could be found in the X-ray pattern. It is not unnatural that the alteration should be confined to a thin surface layer, because if the transformed material has a lower shearing strength than the original, when once a film of the

altered material had been formed plastic deformation will be confined to this film, and the transformation will not spread further.

There were a few definite cases of transformation throughout the mass of the disc. The first results were negative. The apparatus had been constructed in the confident hope that a black form of sulfur would be found analagous to black phosphorus, but none was found. Neither was there a transformation from graphite to diamond. The first positive result was with red phosphorus. The ordinary "violet" phosphorus is transformed irreversibly into black at a pressure of 40000 kg/cm^2. Dr. Jacobs was so kind as to establish for me by X-ray analysis that it was the ordinary black variety; there is at least one other black modification.

An especially promising field for permanent changes appeared to be offered by those substances which are known to exist as minerals in nature in two or more crystalline modifications. One might anticipate that it might be possible to transform the less dense modification irreversibly into the more dense modification. Accordingly a list of such minerals was compiled from International Critical Tables and Mr. David T. Griggs very kindly procured a number of specimens through the courtesy of Professor C. Palache of our University Museum. The following substances were tried: chalcocite, the form of Cu_2S of density 5.6, the usual form being cubic of density 5.78; marcasite, rhombic form of FeS_2 of density 4.87, the usual form being pyrite of density 5.00; andalusite and sillimanite, forms of $Al_2O_3SiO_2$ of respective densities 3.2 and 3.23, the densest form being cyanite of density 3.6; mullite, a less dense synthetic form of $3Al_2O_32SiO_2$; lepidocrosite, a form of $Fe_2O_3.H_2O$ of density 4.09, there being another form goethite of density 4.28, and calcite, the usual form of $CaCO_3$ of density 2.71, aragonite being another form of density 2.93.

Of these the most striking change was produced in chalcocite. Dr. Jacobs found a complete transformation to the ordinary cubic material; none of the X-ray lines of the original were shown at all by the residue after the exposure to pressure and shearing, and instead there were eight strong lines identical with those of ordinary cubic Cu_2S. Cu_2S may be synthesized explosively by shearing stress from the elements copper and sulfur. The product formed in this way gives the lines of both chalcocite and the cubic form. The residues from sillimanite, marcasite, and lepidocrosite were analyzed by X-rays by Drs. Greninger and Hultgren. They found no lattice change, but the lines were considerably more diffuse, indicating a much reduced grain size. There was apparently a transformed metallic surface layer on

one or two of these, which Dr. Greninger was able to positively identify in the case of marcasite as α iron, doubtless rubbed off the steel surfaces.

Calcite was tested twice, but no X-ray analysis was made of the result. There was an obvious increase of density, shown by the floatation method, but any possible change to aragonite was not completed, for the density of the resultant product was somewhat less than 2.84, against 2.93 for aragonite and 2.71 of calcite. There was no apparent abrasion of the steel by this substance. Part of the material after the experiment was left as a film adhering to the steel parts so tightly that it could not be scraped off with a knife, apparently wetting the steel around the edges like the borax glass, and of a hardness obviously considerably much higher than that of the original calcite.

In addition to these one might anticipate the possibility of such transformations as quartz glass to some crystalline form of SiO_2. X-ray analysis by Dr. Greninger showed faint lines of α-crystabolite, but these were already known to occur in quartz glass from his previous work. Determination of density by the floatation method showed a slight increase of density, but this might have been explained by the presence of a slight amount of abraded iron, the presence of which was suggested by a surface blackish discoloration. Any crystallization of this substance under the conditions of these experiments is therefore probably slight in amount, if indeed it occurs at all.

In addition to the substances just mentioned, a number of other specimens were subject to X-ray analysis by Drs. Greninger and Hultgren, and a few cases of change of lattice type established. These were MnO_2, $CaSi_2$, Sb_2O_3, probably $PbCrO_4$, $HgCl_2$. In addition ZnS, which was originally ordinary chemical stock showing the lines of both sphalerite and wurzite, after shearing showed the lines of only one of these modifications.

More interesting than these permanent changes of lattice are chemical decompositions produced by shearing and pressure. One of these has already been mentioned, Bi_2O_3. Measurements of the electrical resistance showed a change from an insulator to a substance with metallic conductivity, suggesting the setting free of metallic bismuth. These electrical measurements merely confirmed the conclusions that had already been reached from an examination of the product of the shearing experiments. The surface was covered with a thin metallic film; abraded steel would not be expected because the shearing strength was not particularly high. Dr. Jacobs found in the residue a couple of the lines of metallic bismuth; these lines were

enhanced in strength by annealing the product to a moderate temperature to permit recrystallization and therefore a larger grain size

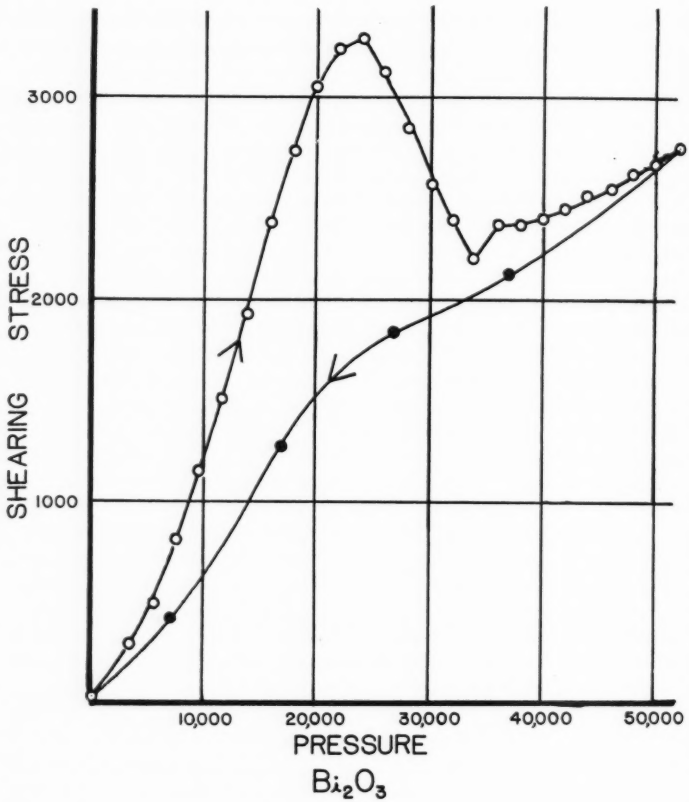

FIGURE 8. The shearing curve of Bi_2O_3. The maximum with increasing pressure probably marks the point where decomposition to metallic bismuth begins. Both ordinates are in kg/cm².

in the metallic bismuth. The character of the shearing curve of itself offers very strong evidence for the decomposition. This is shown in Figure 8. The very striking maximum with increasing pressure,

of which there is no trace with decreasing pressure, is almost certainly due to the setting free of a film of metallic bismuth. The probability of this interpretation is increased by the fact that no polymorphic transition could be found with the volume apparatus. A polymorphic transition sometimes in other cases has been found in conjunction with a shearing curve with similar shape; however, in these cases the curve was retraced with decreasing pressure.

It is probable that at least two other bismuth compounds decompose in the same way to metallic bismuth. The shearing curve of Bi_2S_3 falls steadily and continuously from 30000 on, and the absolute magnitude of the shearing stress over the upper end of the curve is practically the same as for Bi_2O_3. The residue was metallic in appearance. $BiCl_3$ also gives a shearing curve approximately horizontal beyond 35000, of the same absolute magnitude as the curves for Bi_2O_3 and Bi_2S_3, and with no trace of this horizontal part on release of pressure. The evidence in the case of $BiCl_3$ is, however, somewhat less satisfactory than for the other two because of the very rapid absorption of moisture from the air.

Some of the mercury compounds show phenomena like those of the bismuth compounds. HgCl produced an appearance like amalgamation in patches on piston and anvil (it is known that clean iron amalgamates), and the shearing curve fell beyond 35000 kg/cm^2. HgI gave a falling curve beyond 30000, the absolute magnitude being very nearly the same as for HgCl, with no trace of this episode on releasing pressure. There was a metallic looking residue which gave a distinctly metallic streak on paper, so that it is highly probable that free mercury was present. It is probably that the decomposition is to free mercury and $HgCl_2$ and HgI_2 respectively. $HgCl_2$ and HgI_2 show no trace of these effects. $HgSO_4$ and Hg_2SO_4 both behave in essentially the same way. At 30000 the shearing curve reaches a very well marked maximum and beyond decreases continually. On release of pressure the curve of Hg_2SO_4 falls continuously with no maximum. The curve of $HgSO_4$ on the other hand rises slightly, by 3 or 4 per cent, against the 27 per cent fall from the maximum under increase of pressure. The residue in both cases is black on the surface, probably from very finely divided mercury. Investigation of $HgSO_4$ with the volume apparatus showed no polymorphic transition corresponding to the very striking maximum of the shearing curve.

Ag_2SO_4 has a highly unusual shearing curve, practically constant beyond 15000 kg/cm^2 with an abnormally low value of shearing strength. A small and somewhat doubtful transition was found in the

volume apparatus, but even if there were a transition, it would not be expected to affect the shearing curve over such a wide range. In this case there was no obvious change in the appearance of the residue. Li_2SO_4 also has an unusual type of shearing curve, practically constant between 20000 and 40000, and above 40000 gentle rise, concave upward. No transition was found in the volume apparatus. The only unusual feature in the residual product was that it adhered to the steel pistons with unusual tenacity.

SnO_2 was transformed throughout its entire mass from a white to a black substance. Dr. Jacobs found on examination no trace of the lines of the original SnO_2 but only lines of SnO. It is possible that this irreversible transition was produced at comparatively low pressures, because the only feature in the shearing curve was a rather sharp upward bend at about 13000.

Some of the other metallic oxides are also probably permanently changed. The changes in the lead oxides have already been discussed in the original paper. The detonation of PbO_2 there mentioned I am satisfied was a mechanical effect. The experiment was repeated, starting with a film thin enough to avoid detonation. The residue had a superficial metallic appearance, suggesting decomposition to free lead, but the conclusion is uncertain because the shearing strength of this material is so high as to admit the possibility that there may have been abraded iron. PbO, on the other hand, shows a shearing strength on the average six times smaller, and it is very much more probable that the metallic surface lustre found with it must mean free lead. Two experiments with PbS gave similar appearing surfaces strongly suggesting a deposit of free lead.

In addition to the substances already described, a great many others indicated by their appearance some sort of permanent change. Most frequently the indication consisted in a change of color. It was not uncommon to find a few flakes of material with altered color surrounded by unaltered material. The quantity of transformed material was usually very small, too small to attempt to identify by X-ray analysis. $RbIO_3$, for example, showed several reddish brown flakes, the original material being white, but it was not possible to find the explanation of the discoloration by X-ray analysis. Cases of probable transformation produced in this way will be mentioned in the following presentation of detailed data.

It is a question how much of the original data should be given in the following. The curves are not exactly reproducible, but the qualitative features are significant, such as breaks, or the location of the

"knee," etc., so that it seems necessary to give enough to permit a rough construction of the original curve. I have adopted the plan of giving first after the name of the compound the values of the shearing stress, expressed in thousands of kg/cm,^{2} respectively at mean hydrostatic pressures of 10000, 20000, 30000, 40000, and 50000. For example, the entry will be found: FeS_2 (pyrite): 2.3, 6.3, 9.8, 11.5, 12.6 etc. From this it can be read, for example, that the shearing strength of pyrite at 30000 is 9,800 kg/cm^2. These co-ordinates of the curve are then followed by a description of characteristic features; one of the most important of these is the character of the rotation, because this has a connection with the crystal system. Permanent changes of color or other evidence of permanent change are also important. It did not appear feasible to compress all this material into tables because of the greatly varying nature of the comment required. The following summary contains not only the 250 compounds not yet published in any form, but also data for the elements, some of the details for which have already been published in the first paper; there was not space in the first paper to give some of the details now presented. Reference must be made to that paper in order to obtain a complete description of the behavior of the elements. The arrangement in the following is in order of atomic weight.

Detailed Results

Lithium

Li, metal. Shearing curve and other details in first paper.

LiF. 2.3, 5.6, 8.1, 9.7, 10.8. Rotation smooth. Light brown discoloration of steel parts, which is not uncommon with fluorides.

LiBr. 1.3, 3.0, 4.2, 5.4, 5.9. Rotates with snapping and chattering beyond 10000, which at first becomes more violent with increasing pressure, then becomes less violent, and entirely ceases beyond 40000.

$LiNO_3$. 1.3, 3.6, 5.3, 6.5, 7.4. Rotates quietly.

Li_2SO_4. 2.0, 3.9, 3.9, 4.0, 4.4. Rotates quietly. Adheres very tightly to steel.

Li_2CO_3. 0.9, 2.5, 3.6, 3.9, 4.0. Rotates quietly.

Beryllium

Be, metal. 1.6, 3.8, 5.5, 6.6, 7.4. Rotates quietly.

Boron

B, element. 2.2, 4.6, 7.4, 10.6, 18.0 (readings with decreasing pressure). Very violent snapping on rotation. See first paper.

B_4C. 1.7, 5.0, 8.1, 9.8, 11.2. Rotates with violent snapping over entire range. Steel surfaces deeply scratched.

H_3BO_3. 0.3, 1.3, 2.9, 4.5, 5.6. Rotates smoothly.

Carbon

C (graphite). 2.9, 4.7, 6.9, 9.0, 9.9. Rotates with increasingly violent snapping beyond 10000. See discussion in text.

Sodium

Na, metal. 0.2, 1.0, 2.2, 3.6, 5.2. Rotates quietly. See first paper.

NaF. 1.5, 3.9, 5.6, 5.9, 5.9. Rotates quietly. No transition found in volume apparatus although the flat part at the upper end of the curve suggests it. This feature of the curve was checked by repetition. Brown discoloration of steel.

NaCl (natural crystals). 0.9, 1.8, 2.2, 2.4, 3.0. Rotates quietly.

NaI. 0.8, 1.8, 3.0, 3.8, 4.6. Rotates smoothly.

$NaClO_3$. 1.1, 3.1, 3.9, 4.3, 4.2. Sharp drop at 40000, probably due to transitions, of which there are two, which were studied in the volume apparatus. Rotates with chattering and snapping up to 40000, beyond which it is quiet.

$NaBrO_3$. 1.0, 2.8, 3.8, 4.3, 4.6. Rotates with squeaking and snapping up to the knee, at which it ceases entirely. This knee also marks a transition, which was studied in the volume apparatus.

$NaIO_3$. 1.1, 2.5, 4.4, 5.1, 5.7. Rotates quietly. Slight yellow discoloration of residue. No transition found in volume apparatus.

$NaClO_4$. 0.8, 2.0, 2.7, 3.4, 3.8. Rotates scratchily in the region between 25000 and 37000; smooth elsewhere. Transitions studied in the volume apparatus. The shearing curve has minor irregularities which suggest the transition, although they are hardly in evidence on the scale of this reproduction. Residue is brownish red toward the outside of the discs.

$NaIO_4$. 1.6, 3.5, 4.6, 5.4, 6.0. Slight tendency to squeak on rotation, but is mostly smooth. Reddish brown patches in residue.

NaOH. 0.5, 1.1, 2.0, 2.6, 3.2. Rotates quietly.

$NaNO_3$. 1.3, 2.4, 2.9, 3.3, 3.5. Rotates quietly.

$NaNO_2$. 0.8, 1.7, 2.7, 3.2, 3.8. Rotates smoothly. Break in direction at 14000, probably too slight to show on this scale, indicates a transition, which was studied further in volume apparatus.

Na_2SO_4. 1.4, 3.7, 5.4, 6.3, 7.0. Rotates smoothly. At higher temperatures there is a transition which was studied in the volume apparatus; no trace of it at room temperature. The residue has a brownish discoloration, as does also the steel parts.

Na_2SO_3. 1.7, 4.7, 6.2, 6.6, 7.1. Chatters when rotated rapidly, quiet when slower. No transition found in volume apparatus. Light brown discoloration on steel.

Na_2CO_3. 1.4, 3.9, 4.0, 4.7, 5.2. Rotates quietly.

$NaHCO_3$. 0.8, 3.1, 4.5, 5.2, 5.7. Rotates smoothly, except for a light snapping at 7000, probably not significant.

NaCN. 0.8, 1.5, 2.2, 3.0, 3.7. Rotates smoothly.

NaSCN. 1.0, 1.7, 2.1, 2.5, 2.9. Rotates with light snapping beyond 46000; otherwise smooth. No transition found in volume apparatus.

$NaBO_2$. 2.4, 7.2, 9.5. Beyond 30000 the curve dropped, doubtless due to fracture of the steel pistons, which were so badly ground and chewed up that higher readings were not feasible. Rotation always accompanied by violent snapping.

Na_2WO_4. 1.2, 3.4, 4.7, 5.6, 6.6. Rotates smoothly.

$Na_2Cr_2O_7$. 1.2, 2.1, 2.7, 3.2, 3.7. Rotates smoothly.

Na_2HPO_4. 1.7, 3.9, 4.9, 5.5, 6.2. Slight tendency to snap below 7000, rotation quiet above. Residue adheres tightly to steel.

Magnesium

Mg, metal. 0.57, 0.71, 0.75, 0.80, 0.87. See first paper.

MgO. 1.4, 4.7, 7.1, 9.1, 10.9. Rotates quietly except for very infrequent slight snapping. Might not be expected in a substance with so high a shearing strength, and is doubtless a result of the cubic structure.

MgF_2. 2.6, 5.7, 8.3, 10.0, 11.4. Snaps with increasing violence beyond 10000. Residue discolored black on surface, probably abraded steel. Surface of steel has dark brown irridescence.

$MgCO_3$. 2.0, 4.6, 6.9, 8.2, 9.0. Readings made with both increasing and decreasing pressure and were very consistent. Rotation quiet except between 38000 and 22000 on releasing pressure.

Aluminum

Al, metal. 1.0, 1.6, 2.1, 2.6, 3.1. Rotation quiet. Fairly good agreement between increasing and decreasing readings; those given are mean readings.

Al_2O_3. 2.7, 5.5, 7.8, 9.5, 9.4. Rotates with snapping. Residue deeply ground into steel.

Al_2S_3. 2.2, 5.6, 8.9, 9.8, 10.8. Rotates with snapping up to 40000, beyond which it was quiet. There was a detonation at the maximum, probably mechanical. Residue black; appears as if fused to the pistons in places.

Silicon

Si, element. 1.0, 2.4, 4.7, 6.9, 8.8. Results mean of increasing and decreasing pressure. Rotation always with much grinding and snapping.

SiO_2, glass. Quantitative measurements not made. See discussion on page 00 of this paper for the possibility of permanent changes.

Phosphorus

P, black. 1.5, 3.0, 4.7, 6.7, 8.5. Readings all with increasing pressure, decreasing readings lie notably higher. Rotation always with much snapping. See page 424 of this paper for transformation of red phosphorus into black by shearing under pressure.

Sulfur

S, element, crystallized. 1.8, 3.3, 4.7, 6.0, 7.1. Readings with increasing and decreasing pressure practically identical. Rotation always smooth. Residue is sticky, like amorphous sulfur; the identity of the increasing and decreasing curves would indicate that the transition to amorphous had occurred at a very low pressure.

Potassium

KF. 1.6, 3.4, 4.5, 5.3, 6.2. Rotates smoothly. Decreasing readings nearly retrace increasing.

KCl. 0.6, 1.2, 2.2, 2.7, 3.2. Rotates always smoothly. There is an upward bend at 16000 not reproduced by the figures given which corresponds to a transition which has already been studied.

KBr. 0.6, 1.2, 2.2, 2.8, 3.3. Rotation always smooth. An upward bend at 15000, not reproduced by these figures, corresponds to a transition already studied.

KI. 0.7, 1.5, 2.2, 2.9, 3.6. Rotation always smooth. A transition with fairly large volume change is known to exist near 20000, and has already been studied in the volume apparatus. There is only a very slight trace of it in the shearing curve, much less obvious than the corresponding transition of KCl and KBr.

$KClO_3$. 1.5, 3.0, 4.2, 5.1, 5.7. Smooth rotation to 28000, beyond which there is chattering and snapping. There is a transition at 6000 which has been studied in the volume apparatus. There is no particular evidence for a trasition from the shape of the shearing curve; the change in character of rotation at 28000 is doubtless connected with passing the knee.

$KBrO_3$. 1.2, 2.5, 3.4, 4.0, 4.7. Chatters and squeaks up to 40000,

beyond which it is quiet. Discontinuity in direction near where it begins rotating quietly. Transition studied in volume apparatus.

KIO_3. 1.2, 2.8, 3.7, 4.3, 5.0. Rotates scratchily up to 11000, beyond which it is smooth. Transition at this point, studied in volume apparatus.

$KClO_4$. 1.3, 2.4, 3.1, 3.8, 4.3. Rotates smoothly. No transition found in volume apparatus.

KIO_4. 1.3, 2.8, 3.9, 4.7, 5.3. Rotates with spasmodic snapping up to 26000, beyond which it is quiet. There is a break in the shearing curve near 18000, which is not shown well on the above scale. Transition studied in volume apparatus.

KNO_3. 1.0, 2.1, 2.9, 3.6, 4.3. Rotates quietly to 16000, then intermittent chattering to 32000, then quiet again. There is a transition at very low pressures, too low to show on this curve, which has been previously studied. Examination with the volume apparatus shows no other transitions at higher pressures than 12000.

KNO_2. 0.3, 1.2, 1.7, 2.2, 2.6. Rotation smooth throughout. Below 10000 there is a break in direction of the shearing curve, suggested by the co-ordinates given. The corresponding transition has already been studied.

K_2SO_4. 1.3, 3.2, 5.2, 6.4, 7.3. Rotates smoothly.

K_2CO_3. 1.0, 2.2, 2.9, 3.3, 3.7. Rotates smoothly.

$K_2Cr_2O_7$. 1.1, 2.1, 2.7, 3.3, 3.9. Rotates smoothly. Yellow stain on steel, probably powder ground in.

K_2CrO_4. 1.2, 3.1, 4.6, 5.2, 5.6. Rotates smoothly.

K_2MnO_4. 1.1, 2.9, 3.9, 4.5, 5.2. Rotates smoothly. Residue has a putty-like consistency. Green discoloration on steel.

$KMnO_4$. 1.0, 1.7, 4.1, 6.0, 7.5. Rotates smoothly throughout. Sharp upward break at 21000. Corresponding transition studied in volume apparatus. Dark discoloration on steel.

K_2MoO_4. 0.7, 1.4, 1.8, 2.3, 2.8. Rotates smoothly.

$KSbO_3$. 1.5, 2.8, 3.7, 4.7, 5.5. Rotates smoothly.

$KAsO_2$. 1.6, 3.3, 4.3, 5.1, 5.6. Rotates smoothly. Residue hard and tenacious.

KCN. 0.6, 0.9, 2.0, 2.5, 3.1. Rotates smoothly throughout. Sharp upward break at 22000. Corresponding transition examined in volume apparatus.

Calcium

Ca, metal. 0.75, 1.04, 1.30, 1.53, 1.78. Rotates smoothly. Close agreement between points with increasing and decreasing pressure.

CaO. 2.3, 6.1, 9.2, 11.3, 13.4. Rotates smoothly up to 15000, with occasional snapping beyond.

CaF_2. 2.0, 5.5, 9.0, 11.3, 12.7. Rotates smoothly except for one or two snaps. Curves with increasing and decreasing pressure practically coincident. Dark discoloration of steel.

CaI_2. 0.5, 1.2, 1.9, 2.6, 3.2. Smooth rotation. Increasing and decreasing readings practically coincide.

CaS. 2.5, 6.5, 9.8, 10.8, 11.5. Rotates with occasional snapping up to the knee at 30000, and is mostly smooth beyond. Powder ground into steel.

$CaSO_4$, anhydrous. 1.5, 4.2, 6.7, 8.0, 8.6. At the knee at 35000 the character of rotation changes from chattering and snapping to chattering only. Residue adheres tightly to steel.

$CaSO_4.2H_2O$. 1.0, 1.6, 2.8, 4.3, 5.1. Rotation smooth throughout. Sharp upward break at 26000 suggests a transition, which has not yet been investigated in volume apparatus.

$CaCO_3$. 1.8, 4.1, 5.8, 6.9, 7.8. Rotation smooth except for one snap at 13000. Residue adheres very tightly to steel, and the steel shows signs of abrasion. A shearing curve very similar to this was obtained with Solenhofen limestone.

$Ca_3(PO_4)_2$. 2.2, 5.5, 7.5, 8.6, 9.7. Rotates with occasional snapping up to the knee at 25000, smooth beyond. Considerable abrasion of steel surfaces.

$CaSi_2$. 2.1, 5.2, 8.6, 11.5, 13.8. Rotates with violent jumping and snapping over entire range. Steel somewhat abraded, but the damage to the steel was surprisingly little in view of the violence of the jumping and the magnitude of the shearing strength. Dr. Greninger finds the lattice entirely transformed to a new unidentified one.

Titanium

Ti, metal. 1.1, 2.9, 5.5, 9.2, 13.0. Coordinates given are with increasing pressure. Falling curve lies appreciably above rising curve but is still concave upward, an unusual feature. Rotation accompanied by occasional snapping over entire range.

TiO_2. 2.5, 7.0, 9.9, 12.0, 14.5. Rotates smoothly to 11000; beyond that varies spasmodically from smooth to snapping. Abrasion of steel unusually severe.

Vanadium

Va, metal. 2.9, 6.0, 7.6, 10.3, 13.0. Rotates smoothly. Sharp upward break at 32000 suggests transition, not yet investigated in

volume apparatus. Damage to the steel unusually great. Other details in first paper. There is an apparent discrepancy between the two accounts, in that in the first account the statement is made that rotation was occasionally accompanied by snapping. The snapping was entirely confined to the readings with decreasing pressure, and it now seems probable to me that this was due to detached particles of steel. The co-ordinates above are for the increasing branch; in view of the damage to the steel the decreasing branch can probably be ignored.

Chromium

Cr, metal. 3.0, 6.0, 8.4, 10.5, 12.2. Rotation always smooth. Other details in first paper.

Cr_2O_3. 2.3, 6.0, 8.1, 11.0, 13.4. Rotates smoothly to 14000, jumpy beyond that, becoming so jumpy at the upper end that the proper value is very uncertain. An inconspicuous upward break near 28000 is probably verified in the volume apparatus, although the volume change is small. Residue is green toward the center and black at edges. A second run gave a break at the same place.

$CrCl_3$. 2.4, 4.8, 6.1, 7.1, 8.3. Rotates with some chattering up to 11000, beyond which it stops.

$Cr_2(SO_4)_3$. K_2SO_4. $24H_2O$. 0.6, 0.75, 1.04, 1.8, 2.6. Rotation always smooth. Sharp break at 8000 suggests a transition, which has not yet been checked with volume apparatus. Co-ordinates given are with increasing pressure; curve for decreasing pressure falls below over its entire length, with the break at about 22000. This relative location of the two curves is unusual.

Manganese

Mn, metal. 1.6, 3.0, 5.5, 8.9, 11.5. Coordinates for increasing pressure; falling curve lies somewhat above rising curve. Definite upward break at 25000 suggests a transition not yet checked in volume apparatus. Other details in first paper.

MnO. 2.5, 5.7, 8.6, 10.3, 11.8. Rotates smoothly to 27000, occasional snapping beyond. Sharp downward break at 36000 suggests a transition, not yet sought for in volume apparatus. Steel abraded, but with no discoloration. X-ray pattern shows no evidence of metallic Mn.

Mn_3O_4. 1.1, 4.8, 8.4, 10.4, 11.3. Rotates with snapping beyond 12000. Definite upward break at 10000 suggests transition, not yet searched for with volume apparatus. Residue tightly adherent to steel, which is discolored brown.

Mn_2O_3. 1.3, 2.9, 5.5, 8.9, 11.0. Snapping most intense in range between 18000 and 38000. At the highest pressures snapping can be made to vanish by rotating slowly enough. Distinct upward break near 25000 suggests transition, not yet explored for with volume apparatus. Residue is tightly adherent to steel and gives off a distinct odor suggesting acetylene. Patches of brown discoloration on steel.

MnO_2. 2.3, 6.9, 10.9. Snapping was so violent that readings were not attempted beyond 35000. This substance has one of the highest shearing strengths of those measured. Residue adheres tightly to steel, which has a brown discoloration. Dr. Jacobs finds three or four lines of the cubic MnO in the X-ray pattern. Lines so diffuse that any faint lines due to metallic Mn would have been obscured.

MnS. 1.4, 4.0, 6.3, 7.7, 8.6. Rotates quietly to 10000, then with increasing snapping, which becomes markedly less again beyond 37000. Residue so tightly adherent to steel that it cannot be scraped off with knife.

$MnCO_3$. 2.4, 5.3, 6.9, 7.8, 8.5. Rotates with snapping to the knee at 26000, beyond which it is quiet. Residue tightly adherent to steel.

Iron

Fe. metallic. 1.1, 5.2, 8.0, 10.0. Co-ordinates for increasing pressure. Rotates smoothly. Other details in first paper.

Fe_2O_3. 2.3, 6.9, 10.9, 14.0, 16.7. Snapping most intense in the range up to 28000, only occasional above that. Much damage to steel, to be expected from high shearing strength.

FeS_2 (pyrite). 2.3, 6.3, 9.7, 11.5, 12.5. Rotates with chattering and snapping in range from 13000 to 35000; quiet outside this range. Much roughening of steel parts.

FeS_2 (marcasite). 1.7, 5.2, 8.4, 10.8, 12.4. Rotates with continually increasing violence of snapping beyond 10000. Permanent alteration to pyrite might be expected because of the densities. X-ray analysis by Dr. Hultgren shows no lattice change, but the lines are more diffuse.

FeS. 2.0, 6.0, 9.2, 11.0, 11.9. Rotates quietly to 38000, occasional snapping beyond. Abrasion of steel.

Nickel

Ni, metal. 1.0, 2.8, 5.2, 7.5, 8.7. Co-ordinates for increasing pressure. Rotates smoothly. Adheres tightly to steel. Other details in first paper.

NiO. 2.2, 6.2, 8.9, 10.7, 11.9. Rotates smoothly.

Ni_2O_3. 1.7, 5.5, 8.3, 9.9, 11.0. Rotates smoothly.

NiS. 0.9, 1.7, 2.8, 3.9, 4.8. Rotates smoothly. Inconspicuous upward break near 23000 suggests transition not searched for yet in volume apparatus.

$NiSO_4$ (anhydrous). 2.2, 5.9, 8.8, 10.3, 11.4. Rotates with snapping up to 26000, smooth beyond. Brown discoloration of steel.

$NiCO_3$. 2.4, 5.5, 6.5, 6.9, 7.5. Rotation smooth except for occasional snapping at the low pressures.

Cobalt

Co, metal. 0.9, 2.5, 4.0, 5.2, 6.3. Co-ordinates for increasing pressure. Rotates smoothly. Further details in first paper.

$CoCl_3$ (dehydrated). 0.24, 0.42, 0.58, 0.75, 1.00. Notice the unusually low shearing strength. Rotation smooth. Residue blue at center and pinkish toward outside; pink color probably, but not certainly, due to moisture absorbed from air during manipulations.

Co_2O_3. 2.3, 5.4, 8.1, 10.0, 11.7. Rotation smooth.

$CoCO_3$. 1.6, 4.8, 8.1, 9.3, 10.2. Rotates with snapping up to 20000, about the location of the knee, and then smooth beyond.

Copper

Cu, metal. 1.0, 2.3, 3.8, 4.6, 4.9. Coordinates for increasing pressure. Rotates smoothly. Structure so completely destroyed by shearing that Dr. Greninger can find none of the lines of the original metal. Other details in first paper.

Cu_5Sn. 1.5, 3.4, 4.5, 5.0, 5.2. Rotation smooth to the neighborhood of the knee around 25000 and then slight chatter. Residue welded to steel; steel has surface color of Cu_5Sn.

CuZn. 0.9, 1.7, 2.3, 2.6, 2.8. Rotates smoothly. Residue stiff, and not brittle like original. Fuses to steel, which takes surface color of CuZn.

Cu_5Zn_8. 0.41, 0.92, 1.6, 2.2, 2.8. Rotates smoothly. Curve approximately linear to 18000, where there is a definite break upward. Exploration for corresponding transition has not been made with volume apparatus. Residue somewhat malleable. Fused to steel.

Cu_5Cd_8. 0.7, 1.2, 1.8, 2.1, 2.3. Rotates smoothly. Residue stiff and not brittle. Two slight breaks in shearing curves suggest transitions, but the matter has not been examined further with the volume apparatus.

Cu_2O. 2.2, 6.2, 8.2, 9.4, 10.3. Rotates smoothly. Material trapped at center, where it makes a depression in piston and anvil.

Cu_2Cl_2. 0.6, 1.2, 2.0, 2.3, 2.8. Rotates smoothly. Original material probably impure with hydrate, as it was old stock and was light yellowish green, instead of white. Residue is dark brown. Free copper on the steel parts.

$CuCl_2$ (anhydrous). 0.35, 0.75, 1.15, 1.50, 1.88. Rotates smoothly. Free copper on steel parts, thickest toward periphery, where shearing action was most intense.

Cu_2Br_2. 0.46, 1.03, 1.38, 1.64, 2.07. Rotation smooth. Steel parts coated with copper.

$CuBr_2$. 0.34, 0.51, 0.57, 0.68, 0.83. Rotation smooth. Notice very low value of force. Free copper on steel.

$Cu(NO_3)_2.3H_2O$. 0.32, 0.84, 1.51, 2.18, 2.70. Rotation smooth. Increasing and decreasing curves nearly the same. Residue deliquesces so rapidly that properties were not determined.

CuS. 1.3, 3.1, 4.0, 4.5, 4.9. Rotation smooth. Brownish discoloration on steel, which cannot be scraped off; probably metallic copper.

Cu_2S (ordinary cubic modification). 1.5, 2.9, 3.3, 3.6, 4.0. Rotates smoothly. Patches of light brown discoloration of steel.

Cu_2S (natural, chalcocite). 1.6, 2.8, 3.5, 3.8, 3.7. Rotation smooth to 43000, approximately the location of the maximum, and then slight chatter. Dr. Jacobs finds only the X-ray lines of the cubic modification, indicating a complete transformation.

Zinc

Zn, metal. 0.80, 0.92, 1.21, 1.55, 1.84. Rotates smoothly. Distinct upward break at 26000 suggests transition. Exploration with the volume apparatus, both at room temperature and 150° C gave doubtful indications; the change of volume, if there is a transition, is small. Residue fused to steel at edges.

ZnO. 2.1, 6.2, 9.7, 11.0, 12.6. Much snapping beyond 15000, making readings uncertain. Residue brownish.

ZnF_2. 1.8, 3.7, 5.1, 6.1, 6.5. Rotates with violent chattering and snapping over entire range. Abrasion of steel.

$ZnBr_2$. 1.0, 2.0, 1.9, 1.4, 1.1. Rotates smoothly. Very strong maximum at 26000. Transition has been studied with volume apparatus. This material rapidly deliquesces in the air; it was dried by heating over a Bunsen burner immediately before assembling, which was done as rapidly as possible.

ZnS. 1.3, 3.1, 5.0, 7.2, 8.1. Beyond 15000 the snapping becomes rapidly increasingly violent so that the readings beyond 30000 are very uncertain. There seems, however, to be very definitely an upward break in the neighborhood of 26000. This was verified by repetition. Exploration with the volume apparatus disclosed no transition, which may have been suppressed by viscosity, the melting point of this material being comparatively high.

ZnSe. 1.5, 2.8, 3.4, 3.7, 3.9. Rotation always smooth. Increasing and decreasing curves closely coincident. Residue welded to steel.

$ZnSO_4$. 1.9, 4.0, 5.4, 6.0, 6.7. Rotates smoothly. Residue tightly adheres to steel, but dissolves off at once.

$ZnCO_3$. 1.8, 3.9, 5.5, 6.8, 8.8. Rotates smoothly except at very maximum, where there is slight snapping.

Germanium

Ge, element. 1.4, 2.7, 3.9, 4.9, 5.7. Increasing and decreasing curves nearly coincident. Character of rotation unique in that although there was so much jumping as to make readings rather uncertain, there was no noise. Further details in first paper.

GeI_2. 0.7, 1.1, 1.3, 1.7, 2.1. So much chatter beyond 10000 that readings were uncertain; this is unusual in a material of such low shearing strength. The coordinates given are for the increasing curve. This shows a definite downward break at 17000. The decreasing curve does not show this, but everywhere lies below the increasing curve, with unusually large upward concavity. Exploration with the volume apparatus disclosed no transition.

Arsenic

As, metal. 1.8, 4.5, 7.1, 9.3, 11.1. Coordinates mean of increasing and decreasing curves, which coincide closely. Other details in first paper.

As_2O_3. 0.9, 4.8, 6.9, 8.1, 8.9. Rotates smoothly except near 15000 on increasing pressure and below 20000 on decreasing. Residue has brownish discoloration.

As_2S_2. 2.1, 4.0, 5.2, 6.0, 6.7. Rotates with some chattering up to 8000, but is smooth beyond. Residue dark red, showing blue reflections.

Selenium

Se, metallic. 1.5, 2.8, 3.8, 4.7, 5.5. Rotates smoothly. Increasing and decreasing curves practically coincident. Further details in first paper.

Rubidium

RbCl. 1.0, 2.1, 2.8, 3.3, 3.9. Rotates smoothly. A downward break in the neighborhood of 5000, not reproduced above, marks a transition which has already been studied in the volume apparatus.

RbBr. 1.0, 2.2, 2.9, 3.5, 4.0. Rotation smooth. Low pressure transition at practically same place as for RbCl; same remarks apply.

$RbClO_3$. 1.3, 2.2, 3.0, 3.6, 4.1. Rotates smoothly to the knee at 30000, and chatters and creaks beyond. No transition found in volume apparatus. Residue has reddish brown discoloration.

$RbBrO_3$. 0.9, 1.8, 2.5, 3.1, 3.6. Creaks and snaps over most of range. Possible break below 10000. Exploration with volume apparatus disclosed no transition. Residue has distinct reddish brown discoloration toward edges. Steel tarnished.

$RbIO_3$. 1.3, 2.4, 3.2, 4.7, 5.4. Snaps violently over the middle part of the range. This decreases in violence, and near 43000 is replaced by a chattering which has practically disappeared at 50000. Residue has patches of reddish brown discoloration.

$RbClO_4$. 1.1, 2.0, 1.9, 1.1, 1.3. Rotates smoothly throughout. Pronounced maximum at 28000 and minimum at 40000. The same maximum and minimum are shown at decreasing pressure, but less pronounced, and displaced to lower pressures. Transition studied in volume apparatus. No discoloration of residue.

$RbIO_4$. 1.3, 2.2, 2.7, 4.1, 4.9. Sharp upward break at 30000; rotates with much chattering up to the break, where it ceases with dramatic suddenness. Transition studied in volume apparatus. No discoloration of residue.

Strontium.

Sr, metal. 0.6, 0.8, 1.1, 1.4, 2.2. Rotates smoothly except for slight snapping near 50000. Slight upward breaks near 22000 and 35000 suggest transitions, which have not yet been checked in the volume apparatus. Residue tightly adherent to steel.

SrO. 1.8, 5.8, 10.0, 13.0, 14.8. Distinct upward inflection at 13000 suggests transition, which has not been checked in volume apparatus. Rotates smoothly to just beyond the inflection; from here on there are snaps which are very violent if rotation is too rapid, but which almost entirely disappear on slow rotation. Residue is a very hard yellowish film so tightly adherent to the steel that it cannot be scraped off with a knife. Steel shows surprisingly little damage considering the magnitude of the force.

SrF_2. 2.3, 5.8, 8.7, 11.4, 12.1. Rotates mostly with much snapping, which becomes less at the higher pressures and on rotating more slowly. There is some kind of a break near 30000, checked by repetition, which is difficult to characterize more exactly because of the snapping. No exploration in volume apparatus. Steel has irridescent brown discoloration.

$SrCl_2$. 0.9, 2.3, 3.8, 5.1, 5.8. Rotation smooth except for an interval between 24000 and 30000.

$SrBr_2$. 0.7, 1.3, 2.0, 3.0, 3.9. Rotates smoothly to 40000, squeaks and snaps beyond. Strong upward inflection at 27000 suggests transition, which was not found with volume apparatus.

$Sr(NO_3)_2$. 1.4, 3.1, 3.7, 3.8, 3.9. Rotation always smooth. Knee unusually pronounced.

SrS. 1.6, 5.0, 7.3, 8.1, 8.6. Rotates with snapping up to the knee at 35000, smooth beyond. Residue is a light violet. Brownish discoloration on steel, which feels like powder ground into surface when scraped with knife. On standing in the air for an hour, this brown discoloration turns green; it can now be easily scraped off with a knife, leaving the steel bright and untouched beneath.

$SrSO_4$. 2.3, 5.2, 6.9, 7.8, 8.8. Rotates quietly except from between 24000, where there is a downward break more distinct than the usual knee, and 43000, where there is a distinct upward break. No transition found with volume apparatus. Residue tightly adherent to steel, but it can be scraped off with knife, leaving brown discolored steel.

$SrCO_3$. 1.8, 4.6, 6.5, 7.2, 7.8. Rotates smoothly. Practically no effect on steel surfaces.

Yttrium

Yt, metal. 0.74, 1.80, 2.64, 3.54, 4.32. Coordinates for increasing pressure. Slight downward break at 14000, too small to show on this scale. Further details in first paper.

Zirconium

Zr, metal. 1.7, 3.0, 3.7, 4.2, 4.5. Coordinates for increasing pressure. Further details in first paper.

ZrO_2. 1.7, 5.5, 9.5, 10.8, 12.1. Coordinates for increasing pressure; decreasing curve uniformly concave toward pressure axis. Rotates with snapping over the entire range, but this tends to disappear if the rotation is very slow. Seasoning effects unusually large.

Columbium

Cb, metal. 0.6, 1.7, 3.6, 6.2, 9.0. Coordinates for increasing pressure. Further details in first paper.

Molybdenum

Mo, metal. 0.6, 2.4, 5.2, 8.2, 12.1. Coordinates for increasing pressure. Other details in first paper.

MoO_3. 1.7, 4.9, 7.6, 9.6, 11.1. There is a small hump at very low pressure, the coordinate at 4000 being 1.0. Rotates with snapping over the entire range, which tends to disappear on slow rotation. Steel parts are tarnished, with a dull lead-like appearance.

Ruthenium

Ru, metal. 1.3, 3.8, 5.9, 7.8, 9.5. Coordinates for increasing pressure. Further details in first paper.

Rhodium

Rh. metal. 1.2, 2.9, 4.6, 6.5, 8.6. Coordinates for increasing pressure. Other details in first paper.

Palladium

Pd, metal. 2.1, 3.6, 4.5, 5.2, 5.7. Coordinates for increasing pressure. Other details in first paper.

Silver

Ag, metal. 1.0, 2.1, 3.1, 3.9, 4.7. Coordinates for increasing pressure. Other details in first paper.

AgZn. 0.7, 1.4, 1.7, 1.8, 1.9. Rotates smoothly. Residue welded to steel around edges.

Ag_5Zn_8. 0.6, 1.3, 1.8, 2.2, 2.4. Rotates smoothly. Welded to steel around edges. Distinctly less brittle than original.

AgCd. 1.3, 2.3, 2.9, 3.0, 3.15. Rotates smoothly. Welded to steel at edges.

Ag_5Cd_8. 1.1, 2.0, 2.4, 2.6, 3.0. Rotates smoothly. Slight welding at edges.

Ag_2O. 0.9, 1.7, 2.5, 3.1, 3.5. Rotates smoothly. Increasing and decreasing curves practically coincident. No trace of the irreversible effects below 12000 formerly studied.

AgCl. 0.5, 0.7, 0.9, 1.1, 1.3. Rotates smoothly. Slight upward break at 15000. Transition studied in volume apparatus; change of volume very small.

AgBr. 0.5, 0.7, 0.9, 1.2, 1.7. Rotation smooth. Adheres to steel at edges, where the steel is darkened. Upward inflection in

vicinity of 35000 suggests a transition. Examination in the volume apparatus gave doubtful results.

AgI. 0.6, 0.9, 1.15, 1.45, 1.7. Rotation without snapping or other noise, but there was a light grinding feeling to the hand over the entire range. Definite upward break at 3000, too small to reproduce from the above figures, corresponds to transition already studied. Residue ranges from reddish brown to yellow.

$AgClO_3$. 0.6, 1.2, 1.7, 2.0, 2.2. Rotates smoothly. No transition found with volume apparatus.

$AgBrO_3$. 1.1, 1.8, 2.6, 3.0, 3.5. Rotates with much snapping from 5000 to 37000, where it stops. Curve suggests a break downward at 30000. No transition found with volume apparatus.

$AgIO_3$. 1.1, 2.4, 3.2, 3.7, 4.2. Rotates smoothly. Residue glassy in appearance with superficial brown color. Tightly adherent brown residue on steel, which cannot be scraped off with knife, but in water dissolves at once, leaving unaltered steel surface.

$AgClO_4$. 0.8, 1.6, 2.2, 2.6, 2.9. Rotates smoothly. Increasing and decreasing curves closely coincident. Brown residue, rapidly deliquescing.

$AgIO_4$. 1.0, 2.4, 3.6, 3.9, 4.3. Violent snapping up to 13000, where it stops. Suggestion of an upward break where snapping stops. Exploration with volume apparatus gave very doubtful indications of a transition.

$AgNO_3$. 1.7, 2.1, 2.8, 3.4, 3.9. Rotates smoothly with increasing pressure, but there is some tendency to snapping on decreasing. Upward break near 15000 doubtless corresponds to a transition, displaced by shearing stress, already studied. No further exploration was made with the 50000 volume apparatus. Brownish residue adhering to steel.

$AgNO_2$. 0.75, 1.15, 1.7, 3.2, 3.8. Slight tendency to chatter near top; otherwise smooth. Sharp upward break at 33000 corresponds to a transition which was further studied with the volume apparatus. Brown residue.

Ag_2S. 1.5, 2.0, 2.4, 2.6, 3.0. Rotation smooth. Knee at unusually low pressure, below 10000.

Ag_2SO_4. 0.49, 0.57, 0.57, 0.53, 0.54. Rotation smooth. Highly unusual curve. There is a minimum at 45000 more pronounced than would be inferred from the coordinates given; the coordinate at 45000 is 0.51. Transition exploration in volume apparatus gave only doubtful results.

AgCN. 0.20, 0.30, 0.55, 0.95, 1.53. Rotation smooth. Curvature

unusual in being upward over entire range. Exploration in volume apparatus gave doubtful results. Residue mostly yellowish or greenish with a brown tinge at very edge.

Cadmium

Cd, metal. 0.6, 1.0, 1.3, 1.6, 1.9. See first paper for finer details at low pressures, where there are two transitions.

Cd plus Cu or Ag. These intermetallics have been given under the other metal.

CdO. 0.6, 1.8, 3.0, 4.0, 4.5. Rotation always smooth.

$CdCl_2$. 1.0, 2.0, 2.5, 2.8, 3.1. Rotates smoothly up to the knee in the neighborhood of 25000; occasional snapping beyond. Steel somewhat discolored.

$CdBr_2$. 0.25, 0.44, 0.62, 0.93, 1.23. Rotates smoothly.

CdI_2. 0.23, 0.40, 0.53, 0.61, 0.70. Rotation smooth. Decreasing curve slightly below increasing. Light violet discoloration on steel.

CdS. 1.8, 3.6, 4.7, 5.6, 6.4. Smooth rotation. Residue is semi-transparent and red at the edges, getting much darker, with orange patches, near the center. Steel has yellow discoloration, which however does not seem to be an effect of pressure, since the discolored area on the anvil extends beyond the region of contact with the piston.

$CdSO_4$. 1.3, 2.5, 3.5, 4.3, 5.0. Rotation smooth throughout.

Indium

In, metal. 0.13, 0.25, 0.38, 0.54, 0.75. Coordinates mean of increasing and decreasing. Other details in first paper.

Tin

Sn, metal. 0.28, 0.41, 0.60, 0.71, 0.77. Mean of increasing and decreasing pressure, Curve suggests a transition. The exploration in the volume apparatus has been made at both $-78°$ and $150°$ with negative results. Further details in first paper.

SnSb. 2.0, 3.2, 3.3, 3.4, 3.6. Rotation smooth. Knee unusually pronounced. Residue brittle, lightly welded at edges.

$SnCu_5$, see under copper.

SnO. 2.2, 5.3, 8.2, 10.5, 12.7. Spasmodic snapping above 37000, smooth below. No obvious permanent change.

SnO_2. 1.6, 5.1, 8.3, 10.5, 12.5. Rotates smoothly except for isolated snapping at 30000 and 50000. Upward break at 11000. Residue completely altered from white to black, which X-ray

analysis by Dr. Jacobs shows is SnO. Steel surfaces appear to be tinned.

SnS. 0.8, 1.7, 2.2, 2.5, 2.8. Smooth rotation. Steel appears tinned.

SnS_2. 2.0, 4.2, 5.3, 6.0, 6.6. Snaps spasmodically up to 27000, quiet beyond. Steel has brown discoloration.

Antimony

Sb, metal. Curve reproduced and other details in first paper. Rotation smooth.

Sb_2O_3. 2.1, 4.6, 6.6, 7.8, 8.8. Coordinates mean of increasing and decreasing, which nearly coincide. Rotates with snapping to 15000, smooth beyond. Steel discolored, varying from brownish to bluish.

Sb_2O_5. 1.2, 3.0, 4.9, 6.8, 8.6. Rotation smooth. Black film on steel parts which can be scraped off with knife.

$SbBr_3$. 0.75, 1.5, 2.2, 3.0, 3.7. Smooth rotation. No transition found in volume apparatus.

Sb_2S_3. 1.6, 3.6, 4.5, 5.2, 5.8. Isolated snapping at lowest pressures, smooth beyond. Residue ground into steel, which retains a brown discoloration when residue is scraped off with knife.

Sb_2S_5. 1.4, 2.9, 4.0, 4.9, 5.4. Rotation quiet. Slight discoloration of steel.

$Sb_2(SO_4)_3$. 2.0, 3.5, 4.5, 5.3, 5.8. Rotates smoothly. Steel shows evidence of some sort of chemical attack; it is silvery frosted in appearance.

Tellurium

Te, metal. 1.5, 2.2, 3.2, 3.3, 2.8. Rotates smoothly except at very lowest pressure. Coordinates are for increasing pressure. There is a very sharp maximum of 3.6 at 33000. Transitions have been studied in volume apparatus. See first paper for details.

Iodine

I, element. 0.62, 1.54, 2.36, 2.90, 3.11. Coordinates for increasing pressure. Rotates smoothly. Indications for transition doubtful from shearing curve, but transition has been found with volume apparatus.

Caesium

CsBr. 1.3, 2.6, 3.6, 4.4, 5.1. Rotates smoothly.

$CsClO_3$. 0.75, 2.0, 3.3, 4.1, 4.8. Rotates smoothly to 38000, snaps beyond. Upward break at 16000 suggests transition but none was found with volume apparatus. Residue contains a few brown flakes.

$CsBrO_3$. 0.9, 2.4, 3.9, 4.7, 5.3. Chatters and snaps beyond 15000. No transition found with volume apparatus. No obvious change in residue.

$CsIO_3$. 1.0, 2.4, 3.9, 4.6, 5.3. Chattering and snapping begin at 8000, and become more violent for a while; then the snapping decreases and eventually disappears, and at the top the chattering also has nearly disappeared. No transition found with volume apparatus. Residue has reddish brown discoloration.

$CsClO_4$. 0.43, 0.90, 1.8, 2.6, 3.2. Rotation quiet to 48000, where chattering abruptly begins. The strong upward inflection near 20000 suggests a transition, which has been studied in the volume apparatus. No alteration in appearance of residue.

$CsIO_4$. 1.0, 2.3, 3.1, 3.8, 4.6. Rotation quiet. Upward inflection near 36000 suggests transition, of which doubtful indications were obtained with volume apparatus. Residue unaltered except for a flake of purplish brown color, suggesting free iodine.

$CsMnO_4$. 0.8, 1.6, 2.1, 2.8, 3.6. Rotation smooth. Upward inflection at 28000 suggests transition; exploration with volume apparatus not yet made. Residue is gummy in appearance. Nonsoluble brown discoloration on steel.

Barium

Ba, metal. 0.52, 0.71, 0.90, 1.07, 1.20. Coordinates for increasing pressure. Other details in first paper. Rotates smoothly.

BaO. 0.6, 2.4, 3.3, 3.9, 4.5. Rotates quietly except for two snaps near 20000 on decreasing pressure. Residue adheres tightly to steel.

BaF_2. 2.1, 5.9, 8.4, 9.4, 10.1. Rotates smoothly except for two snaps beyond 47000. Steel has brown discoloration.

$BaCl_2$. 1.1, 2.4, 3.0, 3.5, 3.8. Rotates smoothly except for isolated chattering at 8000.

$BaBr_2$. 1.4, 2.6, 3.1, 3.5, 4.0. Chatters over most of the range. The detailed data show a small minimum, not reproduced by the figures just given, near 20000, the significance of which is obscured by the chattering which made readings uncertain. This material gives mechanical detonations with unusually thin discs. No apparent permanent alteration.

$Ba(NO_3)_2$. 1.3, 2.4, 2.9, 3.2, 3.7. Chatters up to the knee at 27000, quiet beyond. Slight brown discoloration of steel.

BaS. 1.6, 4.6, 6.2, 6.7, 7.0. Rotates with snapping up to the knee at 28000, quiet beyond. No transition found in volume apparatus up to 38000 at room temperature. Residue is metallic and dark

brown in appearance, and gives a reddish brown streak on paper, against a very light green streak of the original. Brownish discoloration of steel.

$BaSO_4$. 2.2, 5.8, 7.7, 8.8, 9.5. Rotates with snapping between 18000 and 24000, quiet elsewhere. No alteration in appearance of residue. Brown discoloration of steel.

$BaCO_3$. 2.1, 4.6, 5.9, 6.7, 7.4. Quiet rotation. Residue ground deeply into steel.

$BaCrO_4$. 2.0, 4.5, 6.0, 6.8, 7.8. Rotates with snapping up to 20000, quiet beyond. Residue black. Surface of steel irridescent. Dr. Greninger finds complete change in lattice.

Lanthanum

La, metal. 0.6, 1.15, 2.1, 2.7, 3.1. Rotates quietly. Upward break at 14000. Further details in first paper.

Cerium

Ce, metal. 1.8, 2.3, 2.7, 3.3, 3.8. Sharp downward break at 13000. Rotates quietly up to 13000, much squeaking and chattering beyond. Highly probable that break means transition. Further details in first paper.

$CeCl_3$. 0.6, 2.2, 3.3. Readings not carried beyond 35000 because of fracture of one of pistons. Rotation quiet up to 27000; snapping beyond, probably connected with fracture of steel. No change in appearance of residue.

$CeSO_4$. 1.8, 4.3, 5.9, 6.6, 7.0. Quiet rotation. Residue black, tightly adhering to steel.

Praseodymium

Pr, metal. 0.75, 0.75, 0.85, 1.55, 2.19. Material was highly pure metal which I owe to the kindness of Dr. H. C. Kremers. Rotation was smooth throughout. Character of shearing curve highly unusual, practically horizontal from 8000 to 26000. Coordinates for increasing pressure. Further details in first paper.

Erbium

Er, metal. 0.9, 2.0, 3.5, 5.1, 6.5. Rotation smooth to 45000; snapping beyond 45000 probably due to fragments of steel, the pistons being chewed up much more than usual. Coordinates given are for increasing pressure. Further details in first paper.

Tantalum

Ta, metal. 3.6, 7.4, 8.7, 10.4, 11.5. Coordinates for increasing pressure. Details in first paper.

Tungsten

W, metal. 1.1, 3.1, 5.8, 8.9, 12.8. Coordinates for increasing pressure. Further details in first paper.

WO_3. 2.1, 5.8, 9.3, 12.1, 14.0. Rotates with snapping to 45000, tends to become smooth beyond that. Steel surfaces have a dull lead color.

Rhenium

Re, metal. 1.0, 2.4, 3.9, 5.8, 7.6. Coordinates for increasing pressure. Further details in first paper.

Osmium

Os, metal. 2.5, 5.8, 9.6, 13.4, 17.4. Details in first paper.

Iridium

Ir, metal. 1.15, 3.0, 4.85, 6.6, 8.2. Details in first paper.

Platinum

Pt, metal. 1.8, 3.5, 4.6, 5.4, 5.8. Coordinates mean for increasing and decreasing. Details in first paper.

Gold

Au, metal. 0.7, 1.6, 3.2, 3.9, 4.5. Coordinates for increasing pressure. Details in first paper.

AuZn. 0.8, 2.2, 3.0, 3.6, 4.0. Rotates smoothly to 16000; continually increasing chatter and squeak beyond. Possibly a small break at 25000 not reproduced by figures given. Residue welded to steel around edges.

Mercury

HgO (red). 1.2, 3.1, 4.6, 5.8, 6.8. Rotates quietly. Residue brownish yellow. Light brown discoloration on steel.

HgO (yellow). 1.3, 3.2, 4.9, 6.3, 7.2. Rotates smoothly except for one slight snap at 11000. Residue dark brown. Light brown discoloration of steel and appearance as if lacquered. Color cannot be scraped off with knife. Does not appear certain that there is any essential difference between these two oxides.

HgO (black). 0.8, 2.5, 4.15, 4.9, 5.5. Rotates smoothly. Brown discoloration of steel. Distinct evidences of free mercury in cracks in steel surfaces.

HgCl. 0.90, 1.33, 1.48, 1.51, 1.48. High frequency chattering to 23000, beyond which it stops. Maximum suggests a transition, but none was found with the volume apparatus in the expected

place. Perhaps a transition with very small volume change at low pressures at 150°. Dark deposit on steel which cannot be scraped off with knife. Suggestions of amalgamation.

$HgCl_2$. 1.0, 1.8, 2.1, 2.3, 2.4. Rotates quietly. Transition studied in volume apparatus. Some corrosion of steel parts after run, which, however, appears not to have been an effect of pressure.

$HgBr_2$. 0.23, 0.41, 0.48, 0.67, 0.95. Rotates smoothly. Mechanical detonation at top pressure. Definite downward break at 23000 suggests a transition which was studied further in volume apparatus. Residue so deliquescent and corrosive of steel that no study could be made of possible permanent changes.

HgI. 0.7, 1.15, 1.6, 1.7, 1.65. Rotates smoothly. Results repeat on repetition of set-up. Slight green discoloration of steel.

HgI_2. 0.46, 0.58, 0.69, 0.96, 1.24. Rotates smoothly. Transition corresponding to upward bend at 24000 had previously been studied at higher temperatures and lower pressures,[5] and has now been studied further in the volume apparatus. At the maximum pressure the steel anvil fractured. Residue consists of both yellow and red material. Suggestions of free mercury.

HgS. 1.8, 3.85, 4.8, 5.2, 5.8. Rotates smoothly up to 45000 where there was some snapping, doubtless connected with the rupture of one of the pistons which occurred at 47000. The figure given for 50000 is an extrapolation. Steel darkened. Residue gives a reddish brown streak on paper, distinctly different from the brilliant red of the original, suggesting a permanent alteration.

The experiment was later repeated, this time reaching 50000 successfully without rupture. The coordinates are essentially as given. The permanent alteration of the residue has now evidently proceeded somewhat further. It is black in appearance; the thickest part, from the center where the shearing deformation was a minimum, gives a brown streak on paper, and some of the outer parts give a deep black streak. Evidence seems very good for a permanent alteration.

$HgSO_4$. 1.5, 3.3, 3.55, 3.2, 2.6. Rotation always smooth. No transition could be found in the volume apparatus corresponding to the very pronounced maximum at 28000. Coherent black film on all steel parts, which can be scraped off with knife, leaving steel untouched.

Hg_2SO_4. 1.0, 2.2, 2.5, 2.3, 2.2. Rotation smooth throughout. Curve much like that of $HgSO_4$. Search for transition not yet made with volume apparatus. Residue shades all way from white

through gray to black. Brown discoloration on steel which cannot be scraped off.

In general, with regard to all these experiments with mercury compounds, it seems probable that decomposition to metallic mercury is of frequent occurrence. The unusually frequent serious fracture of the steel would suggest the same thing; this would be an effect of mercury forcing its way into the steel, producing effects similar to those studied many years ago.

Thallium

Tl, metal. 0.22, 0.40, 0.47, 0.75, 1.12. Coordinates for increasing pressure. Further details in first paper.

$TlClO_3$. 1.2, 2.5, 3.45, 4.4, 5.1. Rotates smoothly. Black flakes in residue and an odor like chloride of lime. Dr. Greninger can find no change in the X-ray pattern. Search made with the volume apparatus. No transition at room temperature; on heating to 150° there was an explosion. Residue black, giving completely altered X-ray pattern according to Dr. Greninger.

$TlBrO_3$. 1.15, 2.9, 4.4, 5.3, 5.9. The yield phenomena are unusually complex. Up to 16000 it snaps, with no evidence of plastic flow. Between 16000 and 26000 there is both snapping and smooth flow. Beyond 26000, nothing but smooth plastic flow. Residue is entirely altered in appearance; black metallic flakes. Steel has brown discoloration which cannot be scraped off with knife, but which mostly dissolves away in water. No transition found in volume apparatus. Decomposes at higher temperatures.

$TlIO_3$. 0.9, 2.2, 3.4, 4.2, 5.1. Rotates smoothly except for very infrequent light snapping at lowest pressures. No transition found in volume apparatus. Residue dark metallic flakes. Brown discoloration on steel.

$TlClO_4$. 0.92, 1.14, 1.09, 1.50, 2.04. Rotates smoothly. Maximum of 1.14 at 18000 and minimum of 1.07 at 27000. Transition expected from the shear curve studied in volume apparatus. No permanent change in either residue or steel.

$TlIO_4$. 1.8, 4.5, 6.0, 7.0, 7.9. Rotates with snapping to the knee at 26000 and then smoothly.

Tl_2SO_4. 0.85, 1.62, 1.73, 1.76, 1.91. Rotates quietly throughout. Transition expected corresponding to long plateau, but none found in volume apparatus. Residue is transparent with opaque brown streaks.

Lead

Pb, metal. 0.16, 0.30, 0.44, 0.56, 0.68. Details in first paper.

PbO. 0.65, 1.3, 1.7, 2.0, 2.4. Rotates smoothly. Steel parts have patches of what appears to be free lead.

Pb_3O_4. 2.1, 5.9, 7.0, 7.6, 8.1. Rotates with snapping to the knee at 25000; quiet beyond. Suggestion of free lead in surface of residue.

PbO_2. 1.5, 5.8, 9.9. Readings not carried beyond 27000 (the reading given for 30000 is an extrapolation) because of the extremely violent snapping, which began near 20000. This is the oxide which formerly was found to detonate at 50000 with decomposition; no evidence of free lead found after this run to much lower pressure.

PbI_2. 0.7, 1.5, 2.1, 2.65, 2.95. Rotates smoothly. Inconspicuous inflection at 26000 (the coordinate here is 1.8) suggests transition, which was checked with the volume apparatus. Steel parts suggest the appearance of free lead.

$Pb(NO_3)_2$. 1.4, 2.4, 2.9, 3.05, 3.3. Rotates smoothly.

PbS. 0.50, 0.97, 1.29, 1.44, 1.61. Coordinates mean of increasing and decreasing readings, which coincide very closely. Rotates smoothly throughout. All surfaces appear plated with metallic lead.

PbSe. 1.85, 3.75, 4.7, 4.0, 3.05. Rotates quietly. The coordinate at 50000 is extrapolated. There was a mechanical detonation of the material beneath one piston at 47000. Corresponding to the very pronounced maximum at 30000 a transition was found in the volume apparatus. No evidences of decomposition in residue.

PbTe. 1.5, 2.8, 3.1, 3.0, 2.4. Coordinate at 50000 extrapolated from 47000, where there was a detonation of the material beneath one piston. Rotates smoothly to 43000, where it begins to squeak and chatter. Satisfactory exploration with the volume apparatus has not yet been made. No particular evidence of decomposition.

$PbSO_4$. 0.85, 1.5, 1.85, 2.1, 2.4. Rotation quiet. Inconspicuous downward break at 14000 suggests transition; exploration in volume apparatus not yet made. Evidences of free lead on steel surfaces.

$PbCO_3$. 0.8, 1.8, 1.9, 2.05, 2.1. Coordinate at 50000 extrapolated from 43000, where the anvil broke. Rotates quietly. Slight minimum at 30000 suggests transition; volume exploration not yet made.

$2PbCO_3.Pb(OH)_2$. 0.9, 2.0, 2.2, 2.1, 2.0. Coordinates for increasing pressure; no trace of maximum for decreasing pressure, but curve is nearly linear, slightly concave toward pressure axis. Rotates smoothly. Exploration not made with volume apparatus. Traces of free lead in residue.

$Pb(AsO_2)_2$. 1.7, 3.2, 4.0, 4.8, 5.2. Very violent snapping (which is not to be anticipated because the shearing strength is not particularly high) makes readings uncertain above 20000, where snapping began. This suggests a transition, but no exploration has been made with volume apparatus. Slight suggestion of free lead in residue.

$Pb\ (BO_2)_2.H_2O$. 1.3, 2.5, 3.6, 4.6, 5.3. Rotates smoothly to 30000, with chattering beyond. At 50000 there was a detonation of unusual violence; no residue to examine.

Pb acetate (neutral). 0.45, 0.7, 1.15, 2.2, 3.3. Rotates smoothly except for very infrequent light snapping. Sharp upward break at 27000 indicates transition; no exploration yet made with volume apparatus.

Pb acetate (tri-basic). 0.85, 1.7, 2.3, 2.9, 3.6. Rotates smoothly.

$PbCrO_4$. 1.5, 3.6, 4.45, 4.8, 5.1. Co-ordinate at 50000 extrapolated; detonates at 47000. Rotates with soft chattering up to 23000, and is quiet beyond. Residue ground into steel.

Pb phosphate. 0.8, 1.5, 1.7, 2.05, 2.6. Rotates smoothly. Distinct upward break near 33000 suggests transition; exploration not yet made with volume apparatus.

There seem to have been an unusual number of detonations with the lead compounds. This suggests decomposition to free lead. The shearing strength of lead is known to be very low. If lead were to be suddenly injected into the mass undergoing shear it would become weaker and might permit just that mechanical instability that results in detonation.

Bismuth

Bi, metal. Curve given in detail in first paper.

Bi_2O_3. 1.3, 3.2, 2.65, 2.5, 2.8. Coordinates for increasing pressure. Sharp maximum at 24000 with coordinate of 3.4, and sharp cusp-like minimum at 34000 with coordinate 2.3. Rotates with snapping up to the cusp, and then smooth beyond. With decreasing pressure no trace of maximum or minimum is found, but the curve is smooth, concave toward pressure axis. Dr. Jacobs finds the lines of metallic bismuth in residue. Seems to be no

question but that maximum and minimum are connected with the dissociation.

$BiCl_3$. 0.7, 2.0, 2.4, 2.65, 2.75. Coordinates for increasing pressure. Rotates smoothly to 23000, with chattering beyond. Downward break at 23000 suggests transition, but none was found with volume apparatus. Residue too deliquescent to permit satisfactory examination for permanent change.

BiI_3. 0.7, 1.7, 3.05, 4.7. Detonates at 43000. Rotates with hissing sound (an unusual effect) up to 28000, where it ceases. Residue dark red.

Bi_2S_3. 1.4, 2.1, 2.9, 2.85, 2.75. Rotates quietly, but with more fluctuation than usual in the readings. Suggestion of free bismuth on surface of steel.

Thorium

Th, metal. 1.7, 2.8, 3.8, 4.7, 5.5. Coordinates for increasing pressure. Definite downward break at 7000 and another at 14000. Rotates smoothly. Further details in first paper.

$ThCl_4$. 1.3, 3.0, 4.0, 4.7, 5.3. Smooth rotation.

Uranium

U, metal. 0.7, 2.8, 5.4, 7.3, 8.8. Rotates smoothly. Coordinates for increasing pressure, and for first of two samples. Further details in first paper.

UO_2Cl_2. 0.9, 2.1, 3.0, 3.6. Piston breaks at 41000. Rotates quietly.

Ammonium compounds

NH_4F. 1.3, 2.4, 3.5, 4.3, 5.1. Rotates quietly to 43000, where it starts to squeak.

NH_4Cl. 0.9, 1.8, 2.6, 3.3. Piston cracks at 45000. Rotates smoothly.

NH_4Br. 0.7, 1.5, 2.2, 2.8, 3.3. Ascending and descending curves practically coincident. Rotation smooth.

NH_4I. 0.65, 1.4, 2.2, 3.0, 3.65. Ascending and descending curves practically coincident. Rotates smoothly.

NH_4IO_3. 1.2, 2.6, 3.6, 4.3, 4.85. Rotates smoothly.

NH_4ClO_4. 1.1, 2.1, 2.4, 1.9, 1.8. Sharp maximum of 2.5 at 28000, and round minimum of 1.7 at 45000. Coordinates are for increasing pressure; minimum and maximum also shown with decreasing pressure, but not so pronounced. Experiment was repeated with approximately the same results. Rotation always smooth. Transition studied in the volume apparatus.

NH_4NO_3. 1.1, 2.0, 2.8, 3.5, 4.6. Coordinate at 50000 extrapolated; piston breaks at 43000. Rotates smoothly. There are known transitions at low pressures, which have already been investigated. There is a possible slight upward break near 30000, exploration with the high pressure volume apparatus shows nothing. Residue had patches of brown and yellow discoloration, and there were small patches of similar discoloration on the steel.

$(NH_4)_2SO_4$. 1.3, 2.4, 3.2, 3.9, 4.5. Rotates smoothly.

Ammonia Alum. 0.45, 0.65, 0.8, 1.7, 2.65. Distinct upward break near 33000. Exploration in volume apparatus not yet made. Rotation smooth.

Ammonium phosphate (mono-basic). 0.8, 1.6, 1.9, 2.0, 2.5. Rotates smoothly.

$(NH_4)_2CrO_4$. 1.1, 2.1, 2.8, 3.45, 4.2. Rotates smoothly. Rather abrupt downward break at 15000 suggests transition; exploration not yet made with volume apparatus.

Minerals

Certain of the salts already described occur in nature as minerals. In addition to these the following few others have been studied. The shearing curves of these were determined only incidentally in the course of an investigation as to whether permanent changes of density would be produced to other known denser forms.

Mullite, synthetic. $3Al_2O_32SiO_2$. 1.8, 5.2, 9.0, 10.5, 10.8. Rotates with snapping which at first becomes more violent toward the middle of the pressure range, and then becomes weaker toward the top.

Sillimanite, $Al_2O_3SiO_2$. 2.1, 6.1, 10.1, 11.2, 11.8. Rotates smoothly up to 12000, then with much snapping.

Andalusite, $Al_2O_3SiO_2$. 2.4, 6.7, 10.9, 13.3, 15.4. Rotates smoothly up to 15000, snapping beyond.

Lepidocrosite, $Fe_2O_3.H_2O$. 1.3, 3.8, 6.6, 8.9, 11.4. Rotates smoothly over entire range.

Discussion

Many points have already been discussed; there remain a few points best considered now that the data are all in. In spite of the incompleteness of the results, a statistical study will yield results of some significance. There is in the first place the actual numerical magnitude of the shearing strength at 50000. The extreme range is from 500 kg/cm^2 for Ag_2SO_4 to 18000 for boron, a range of 36 fold. The range is doubtless actually higher, because it is to be remembered

that the highest values do not correspond to internal flow but to surface slip. In any event this method could not yield figures higher than the shearing strength of the hardened steel parts, any stronger substance abrading the steel. The range from 500 to 18000 is not different in order of magnitude from the range of ordinary tensile strength and shearing strength at atmospheric pressure.

As far as the elements are concerned there is a very rough correlation between the shearing strength at 50000 and the melting point, the elements with high melting points tending to have high shearing strengths. This same sort of rough correlation is known to hold at atmospheric pressure between melting points and tensile strength or hardness, and the significance is probably not much different. The elements whose shearing strength lie most out of line with regard to this correlation are on the one hand the non-metallic elements S, As, and P, which have a much higher shearing strength than one would expect from their comparatively low melting points, and on the other hand the metals Ba and Zr, which have a lower shearing strength than one would expect, Zr particularly falling out of line. It would be of particular interest to be able to establish reversals in the order of shearing strength brought about by high pressure, but unfortunately in most cases the data do not exist at atmospheric pressure. It is probable, however, that the alkali metals exhibit an abnormally large increase of shearing strength under pressure. Sodium at atmospheric pressure is one of the softest of the metals but at 50000 has a shearing strength almost equal to that of platinum and palladium and much higher than aluminum and bismuth which are normally very much harder and stronger. Lithium shows the same tendency, although not to so great an extent. In the first paper comment was made on the crossing of the shearing curves of sodium and lithium. The alkali earth metals calcium, strontium, and barium on the other hand do not show this effect, but at 50000 retain their comparatively low shearing strengths.

The substances with the absolutely lowest shearing strengths at 50000 include in the first place the metals indium, tin, and lead. The salts with shearing strengths of 1000 kg/cm^2 or less are Ag_2SO_4, CdI_2, $CuBr_2$, AgBr, and $CoCl_3$. It is tempting to see a correlation between the low value for CdI_2 and its crystal structure, which is that of a layer lattice of molecules, but the extreme disorientation produced by shearing makes of little significance the existence of a single plane of easy shear, as shown for example by the high shearing strength of single crystal graphite after it has been disorganized by

prolonged shearing. It is probable that the coexistence of low shearing strength with this structure in CdI_2 is more or less fortuitous. Some highly unusual effect must be responsible for the very low value of Ag_2SO_4; at low pressures this material will support as high a shearing stress as many others; its abnormally low value at high pressures is a consequence of the fact that its shearing curve does not rise beyond a pressure of 16000.

The substances with shearing strengths at 50000 equal to 13000 kg/cm^2 or more are, in order: Va, Ti, CaO, Cr_2O_3, $CaSi_2$, WO_3, TiO_2, SrO, andalusite, Fe_2O_3, Os, and B. These are all substances with high melting points and high hardness. The only metals in the list, Va, Ti, and Os, were all somewhat suspect with regard to purity. The highest figure found for a metal of unimpeachable purity was 12,700 for tungsten; again there is a correlation with the high melting point. Probably the major significance of this correlation with the melting point is that the approach of melting is roughly anticipated in the solid by an increase of internal mobility.

A frequency curve of shearing strength against numbers of examples is not smooth, but there are three regions of maximum. There is a long swell, starting at the origin, rising to a maximum in the neighborhood of 4000 kg/cm^2 and falling to a minimum at 6500; then a second swell, rising to a maximum near 8500 and falling to a minimum near 10000, and then a third swell, rising to a maximum and then shading off to the highest recorded value, 18000 for boron. The significance, if any, of this distribution is not obvious.

The character of the shearing, whether quiet or not, is of significance. In the detailed data will be found 188 substances that shear quietly over the entire pressure range, 21 which shear with snapping or internal fracture over the entire range, 34 which snap below a certain pressure and become quiet above it, 37 which are quiet up to a certain pressure and snap at all pressures above it, and 6 which snap only in an intermediate range and shear quietly at all pressures either above or below this range. The change from smooth to snapping flow in many cases accompanies a polymorphic transition, as already mentioned. In a smaller number of cases the change in character is accompanied by passing the knee in the curve, where surface slip gives way to internal slip. There are 9 substances which become quiet at pressures beyond the knee and only 3 which are quiet below the knee and become noisy above it; that is, 9 exanples where surface slip is jerky and internal slip smooth, and 3 examples where surface slip is smooth and internal slip jerky. It might be

thought that yield in snapping would occur only in those materials which are brittle or hard under ordinary conditions, and therefore which have a fairly high value of shearing strength. This is true to a certain extent, but flow with snapping may extend a long way toward the weaker substances. $RbBrO_3$ with a shearing strength of 3600 at 50000, or $BaBr_2$ with 4000 are the two substances with lowest shearing strength which snap over the entire range.

It has already been suggested that there must be some relation between the smoothness of the shearing and the number of possible slip planes in the crystal. The crystal blocks must be thought of as

TABLE

Crystal System	Total number of examples	Per cent flowing smoothly over entire range	Per cent snapping over entire range	Per cent snapping only at high pressure	Per cent snapping only in intermediate range
Cubic	84	90.5	3.6	——	6.0
Hexagonal	42	69	14.3	14.3	2.4
O-rhombic	35	66	11.4	14.3	8.5
Tetragonal	13	54	15.4	7.6	23
Monoclinic	5	80	——	——	20
Triclinic	2	100	——	——	——

highly deformed by plastic flow; if each block by itself contains a number of different shear planes, the chances are better that at least one of these will be situated so that shear on it is possible than if there is a smaller number. Now every cubic crystal, no matter what its special type of lattice structure, must have at least three different sets of shear planes if it has any at all, merely in virtue of the equal symmetry of the three axes. No other crystal system has so high a number, so one might anticipate that quiet shearing will be specially likely to occur in cubic crystals. The following table gives certain statistics bearing on this question. Naturally only those substances can be tabulated whose crystal system is known, so that a good many interesting examples have been omitted. The information with regard to crystal system was taken from Wyckoff. In the table those substances which snap only at low pressures have been discarded since this is only a surface phenomenon probably not so intimately connected with the crystal structure as internal slip. Also one cubic

compound which snaps only at high pressure, SrO, has been discarded, because the onset of snapping was correlated with a break in the curve, so that a polymorphic transition is probable. The table makes obvious the greater ease with which smooth flow takes place in cubic crystals. In the list of cubic substances will be found some which have high melting points and are brittle under ordinary circumstances, such as Va, or CaO or CaF_2, which might naturally be expected to rupture in shearing. The comparatively large number of hexagonal compounds which flow with rupture over the entire range is doubtless to be connected with the fact that a large number of hexagonal substances are known to have only a single plane of slip, perpendicular to the hexagonal axis.

The normal shearing curve is concave toward the pressure axis over the entire range. There are about ten exceptions, convex toward the pressure axis. That is, the shearing strength of these substances rises more rapidly with pressure than the pressure itself. In no case, however, is the departure from linearity very great. These are all substances with rather low values of the absolute shearing strength. It is plausible to suppose that this low value of the shearing strength is associated with some abnormal feature of the flow mechanism at low pressures which may tend to become more normal at higher pressures. There is a striking difference between these curves of shearing strength and the curves of viscosity of a liquid as a function of pressure. The latter are always strongly concave upward, the logarithm of viscosity being approximately linear against pressure. This I have explained in terms of an interlocking of the molecules which increases rapidly at high pressures.[6] This interlocking was inferred to be very much more prominent in substances with complicated molecules. It is not unlikely that the elements and simple inorganic compounds studied here have been of too simple a character to permit interlocking to an important extent. It is perhaps significant that the only two organic compounds measured up till now, paraffin and dinitrotoluene, both give shearing curves concave upward.

It is plausible to think that something somewhat similar to the interlocking effect may be present even in simple substances, and it is not unlikely that the increase of shearing strength with pressure is due to an effect of this sort. If the planes which shear over each other during plastic flow have anything corresponding to roughness on the atomic scale, then they must rise and fall to a certain extent during this slip. Because of inequalities in structure and temperature agitation, rise and fall will not be a reversible phenomenon, but there

will be a dissipation of energy during slip, and therefore a force resisting the slip. This part of the force resisting slip, that is, this part of the shearing strength, will obviously be greater the greater the normal pressure, so that in general the curve of shearing strength will rise. The fact that the rise is less rapid than linear in most cases is doubtless connected with the decrease of compressibility with increasing pressure,

It is of some interest to compare the absolute values of shearing strength with those calculated theoretically. It is well known that the shearing strength of substances like NaCl under ordinary conditions is smaller by a factor of 1000 than simple theory demands.[7] This discrepancy has been the occasion of a great deal of theorizing, and is usually explained in terms of some sort of imperfection in the structure, either imperfections in the lattice, or else surface defects. The shearing strength of NaCl at 50000 according to the above data is 3000 kg/cm^2. This corresponds to a tensile strength of 6000 kg/cm^2. The tensile strength as calculated according to the simple theory is usually given as of the order of 20000 kg/cm^2. The approximation to the theoretical value at high pressures is therefore of a different order of magnitude from what it is at low pressures.

The mere fact that flow takes place under the conditions of these experiments has a significant bearing on theories of the mechanism of flow. The flow must take place in parallel layers, parallel to the face of the disc, and must be a completely internal phenomenon. Any theory of flow, therefore, which demands that flow be connected in some way with imperfections in the surface cannot be applicable under these conditions, and therefore cannot be a completely general theory of the process of flow. One would be inclined also to think that internal cavities must pretty much vanish under pressures as high as 50000. Flow must be possible by some sort of mechanism in a homogeneous substance, with no internal cavities, but only the sort of imperfection incidental to the fitting together of crystal blocks of different orientations.

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